INSTITUTE OF
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LOW LIGNIN BLEACHABLE PULPS

Project 3474-1

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

October 15, 1981

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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TABLE OF CONTENTS

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SUMMARY

Experiments have been performed to determine the extent to which the kraft-anthraquinone and kraft processes can be used to pulp to very low lignin contents without detrimental effects on yield or pulp quality. Response surface methodology was used, together with direct search optimization, to minimize kappa number at several viscosity levels. The results show that the kraft-anthraquinone process can be operated in such a way as to effect substantial reductions in unbleached kappa number relative to current commercial practice, and that the kraft process is capable of smaller reductions. For the kraft-anthraquinone process, operating conditions have been identified which may allow a 60% reduction in unbleached kappa number. The low-lignin pulps were more readily delignified by chlorination and caustic extraction than were conventional pulps but were slightly more difficult to bleach to high brightness. Pulps produced at kappa numbers as low as 14 were similar in yield to conventional kraft control pulps but had marginally lower tear strength.

INTRODUCTION

Conventional kraft pulping of softwoods for bleachable grades is normally terminated at kappa numbers of 30 to 35. Production of unbleached pulps having lower lignin contents ("low-lignin pulping") would reduce the amount of lignin which has to be removed in the first two bleaching stages. This would have the twofold benefit of reducing both bleachery effluent pollution potential and bleaching chemical cost. In these respects low-lignin pulping would be analogous to oxygen bleaching if comparable kappa number reductions could be achieved.

Low-lignin pulping may also have other advantages. These include an improved overall mill energy balance as a result of increased recycle of organic materials, a reduction in the amount of screen rejects produced, and improved bleachability in short bleaching sequences. Chlorine-free bleaching sequences might also have an improved chance of being successful if there were less lignin to be removed from the unbleached pulp.

The primary constraints on the degree to which the unbleached pulp lignin content can be reduced are pulp strength and pulp yield. Recovery capacity and digester capacity may also become important factors limiting the degree of delignification in the pulping step. The former must be considered since pulping to lower lignin contents will result in a greater load of organic material to the recovery system. The inorganic load may also increase, depending on the method chosen for reducing the unbleached lignin content. Digester capacity must be considered if the proposed strategy involves the use of longer cooking time. Bleachability may be another constraint if the ease of removal of the residual lignin is adversely affected by the means chosen for reducing unbleached lignin content.

Early in the present study it was recognized that anthraquinone may be a useful route to low-lignin pulps because of the improved selectivity its addition imparts to the kraft process. Accordingly, the potential of the kraft anthraquinone process was investigated by optimizing it for the production of low lignin pulps. Optimum conditions for similarly using the kraft process were also established, both to provide a basis for comparison and to investigate the extent to which kraft conditions can be varied to produce low-lignin pulps in an otherwise conventional process.

Low-lignin pulping has been the subject of recent research in Sweden by Hartler, Teder, and their coworkers (1-4). Their approach involves modification of the time profiles of the concentrations of alkali, hydrosulfide ion, and dissolved lignin during a kraft cook. This was achieved by additions of alkali and withdrawal of liquor during the course of the cook. Our work, on the other hand, has been concentrated on evaluating smaller modifications to existing technology and has included anthraquinone addition as a major variable.

More recently Fossum *et al*. have published the results of a study of the effects of addition of anthraquinone to kraft cooks of Scandinavian pine and birch. They found only a small beneficial effect of anthraquinone addition on pulping selectivity and noted that the effects of AQ in the kraft pulping of these species were lower than have been reported for other species. They did, however, observe a significant lowering of the kappa number at a fixed post-oxygen-stage viscosity level when anthraquinone was added to the kraft cook.

CONCLUSIONS

1. Relative to conventional practice, kappa number reductions of 40-50% are accessible in the kraft-anthraquinone and kraft processes by changing pulping conditions. These reductions are attained without serious losses in pulp viscosity or yield.

2. The resulting "low-lignin" pulps are no more difficult to delignify by chlorination and caustic extraction than are conventional kraft pulps and consequently require less chlorine and caustic.

3. Low-lignin pulps are slightly more difficult to brighten in the final stages of the bleaching sequence. However, the increased requirement for chlorine dioxide would be more than offset by the savings in chlorine and caustic associated with the lower unbleached kappa numbers.

4. The unbleached kappa number of kraft pulp can be decreased to about 20 with no loss in strength. Larger reductions, achieved by adjustment of cooking conditions or by using anthraquinone, cause a loss in tear strength of approximately 10%.

5. Models of the type $y = kX_1^{\alpha}X_2^{\beta}X_3^{\gamma}$ ...... can be used to accurately describe the effects of liquor-to-wood ratio, effective alkali, H-factor sulfidity, and anthraquinone charge on pulp yield, kappa number, and viscosity. This type is an extension of earlier published models to include the effects of liquor-to-wood ratio and sulfidity and should be useful in comparing the behavior of different wood samples as well as in arriving at optimum pulping conditions.

6. At a given cooking time in the kraft and kraft-anthraquinone systems, southern pine pulp viscosity is (a) decreased when effective alkali charge is increased, (b) increased when the liquor-to-wood ratio is increased, and (c) unaffected by anthraquinone charge and sulfidity. At a given kappa number, viscosity (a) only slightly decreases with increasing effective alkali charge, (b) increases with increasing liquor-to-wood ratio, and (c) increases with increasing anthraquinone charge and/or sulfidity.

RESULTS AND DISCUSSION

KRAFT PULPING

Pulping Models

A series of laboratory bomb cooks of southern pine chips was carried out with conditions varied to form a central composite rotatable experimental design (6). The nature of the experimental design is evident from Tables I and IV. The resulting pulps were screened, and the kappa number and viscosity of each of the screened pulps were determined. The results, together with those of yield determinations before and after screening, are shown in Table I.

The data of Table I were subjected to multiple regression analysis after suitable coding (scaling) of the independent variables. This analysis gave four equations relating the four measured dependent variables to the coded variables, their cross products, and squares. At this point statistical tests revealed that the effects represented by many of these terms were nonsignificant. The nonsignificant terms were accordingly deleted from the preliminary equations to give the final equations listed in Table II. These equations, which adequately described the behavior of the process throughout the region investigated, constitute an empirical mathematical model for the kraft pulping of loblolly pine. This model is referred to as the polynomial model to distinguish it from an alternative form described below.

The alternative model was an extension of the type described by Lin *et al.* (7). These authors found that the kappa number of unbleached hardwood kraft pulps could be predicted from the equation, kappa number = $K(L/W)^{\alpha} \cdot EA^{\beta} \cdot H^{\gamma}$. A model of this type was subsequently found by Ghosh *et al.* (8) to adequately describe the behavior

TABLE I

KRAFT PULPING DATA

Cook No.	Time at 173°, min	H-Factor	Effective Alkali, %	Sulfidity, %	Liquor-to-wood Ratio, cc/g	Yield, %	Screened Yield, %	Kappa No.	Viscosity, cp
23.4	60	1445	16	15	3	47.8	47.2	54.3	26.6
22.2	180	3794	16	15	3	42.7	42.7	21.2	15.9
19.7	60	1469	20	15	3	45.0	44.7	32.8	22.4
24.6	180	3822	20	15	3	40.2	40.2	13.3	8.3
22.1	60	1455	16	35	3	45.9	45.7	29.8	31.8
19.1	180	3829	16	35	3	42.2	42.2	15.8	15.5
23.3	60	1445	20	35	3	44.3	43.9	21.1	18.6
19.2	180	3829	20	35	3	38.7	38.7	11.4	7.8
20.4	60	1392	16	15	5	53.4	52.8	94.5	47.8
23.6	180	3832	16	15	5	45.1	44.9	32.9	31.4
20.6	60	1392	20	15	5	48.8	48.6	58.8	35.4
22.3	180	3794	20	15	5	42.1	42.0	19.5	15.7
20.2	60	1392	16	35	5	49.3	48.5	50.8	50.9
19.6	180	3829	16	35	5	44.0	44.0	20.9	27.3
23.5	60	1445	20	35	5	46.2	46.1	34.4	37.0
24.2	180	3822	20	35	5	40.7	40.7	11.9	14.0
24.5	240	5002	18	25	4	40.4	40.4	13.0	11.2
24.4	120	2618	14	25	4	46.7	46.6	34.4	28.2
20.3	120	2572	22	25	4	41.5	41.5	15.0	12.9
22.6	120	2637	18	5	4	45.8	45.8	52.4	20.8
20.5	120	2572	18	45	4	42.2	42.2	17.9	19.8
19.5	120	2649	18	25	2	41.7	40.6	15.6	9.3
24.1	120	2618	18	25	6	50.4	50.3	29.6	28.2
19.3	120	2649	18	25	4	43.7	43.6	20.6	20.3
19.4	120	2649	18	25	4	42.3	42.2	20.9	19.8
20.7	120	2572	18	25	4	44.7	44.7	21.8	22.9
22.4	120	2637	18	25	4	43.3	43.3	21.5	20.4
22.5	120	2637	18	25	4	43.8	43.8	21.8	23.4
23.2	120	2627	18	25	4	43.5	43.5	22.2	19.6
24.3	120	2618	18	25	4	42.8	42.8	20.0	24.1

TABLE II

POLYNOMIAL MODEL FOR KRAFT PULPING OF LOBLOLLY PINE[a,b,c]

Equation	R^2	Coefficient of Variation of Measured Quantity, %: Residual[d]	Replicates[e]
Total yield, % = $43.6 - 2.8X_1 - 1.4X_2 - 0.9X_5 + 1.7X_6 - 0.4X_1X_6 + 0.6X_1^2 + 0.6X_6^2$	0.95	1.8	1.7
Screened yield, % = $43.6 - 2.6X_1 - 1.4X_2 - 0.8X_5 + 1.7X_6 - 0.4X_1X_6 + 0.5X_1^2 + 0.4X_6^2$	0.94	2.0	1.8
ln (Kappa no.) = $3.08 - 0.46X_1 - 0.22X_2 - 0.24X_5 + 0.19X_6 + 0.05X_1X_5 - 0.06X_1X_6 - 0.04X_5X_6 + 0.11X_1^2 + 0.09X_5^2$	0.99	6.5	3.7
ln (Viscosity, cp) = $3.06 - 0.38X_1 - 0.23X_2 + 0.29X_6 - 0.08X_1X_2 + 0.06X_1^2 - 0.05X_6^2$	0.97	9.2	8.7

[a]The independent variables in the above equations are defined as follows:

$$X_1 = \frac{(\text{Time at } 173°\text{C, min}) - 120}{60}$$

$$X_2 = \frac{(\text{Effective alkali}) - 18}{2}$$

$$X_5 = \frac{(\text{Sulfidity}) - 25}{10}$$

$$X_6 = (\text{Liquor-to-wood ratio}) - 4$$

[b]The equations are valid only within the region bounded by $X_1^2 + X_2^2 + X_5^2 + X_6^2 = 4$.
[c]Constant conditions: 90-minute rise to a maximum temperature of 173°C.
[d]Calculated from sum of squared deviations of all data points from the fitted surface.
[e]Calculated from variance of replicate center points.

of kappa number and yield in the soda anthraquinone pulping of hardwoods. The corresponding equations were of the form kappa number or yield $KEA^{\beta} \cdot H^{\gamma} \cdot AQ^{\varepsilon}$.

In the present work the same type of model was found to be applicable to both the kraft and kraft-anthraquinone pulping of southern pine. Furthermore, we have shown that it can adequately describe the effects of both liquor-to-wood ratio and sulfidity in addition to the independent variables included by Lin _et al_. and Ghosh _et al_., and that pulp viscosity can be described by the same type of model. The equations obtained when the kraft pulping data of Table I were fitted to a model of this type are shown in Table III. It is apparent that these equations are a better fit for the yield data than the corresponding equations of the polynomial type, and that the kappa number and viscosity equations are only marginally poorer than those of the polynomial model. Thus, the exponential model provides an adequate fit for the data with fewer fitted constants than the polynomial model.

The goodness of fit of both types of models is evident from the observed and calculated values of all measured properties set out in Table IV. It should be noted that the exponential equations for yield do not apply at extreme values of liquor-to-wood ratio, and that the exponential kappa number equation applies only for kappa numbers less than 55.

The pulping behavior predicted by the polynomial model is graphically detailed in Appendix I. At a given cooking time, the yield is decreased by 1.4% if the effective alkali charge is increased by 2%. Similarly, it is decreased by 0.9% if the sulfidity is increased by 10%. The effect of liquor-to-wood ratio on yield is greater at high ratios and short cooking times. In general, increasing the liquor-to-wood ratio increases the yield, but it also decreases the degree of delignification, as seen below. Kappa number is decreased by increases in the effective alkali

TABLE III

EXPONENTIAL MODEL FOR KRAFT PULPING OF LOBLOLLY PINE

	R^2	Coefficient of Variation of Measured Quantity, %: Calculated from Residual Mean Square	Coefficient of Variation of Measured Quantity, %: Calculated from Replicate Measurements
Total yield, % = $\dfrac{271.1\ L/W^{0.1155}}{EA^{0.2911}S^{0.0394}H^{0.1292}}$	0.96	1.6	1.8
Screened yield, % = $\dfrac{246.5\ L/W^{0.1144}}{EA^{0.2802}S^{0.0389}H^{0.1214}}$	0.95	1.5	1.8
Kappa no. = $\dfrac{1.081 \times 10^{7}\ L/W^{0.6125}}{EA^{1.9327}S^{0.4872}H^{0.8605}}$	0.97	8.2	3.7
Viscosity = $\dfrac{7.699 \times 10^{5}\ L/W^{1.084}}{EA^{2.0574}H^{0.7739}}$	0.95	12	8.7

TABLE IV

COMPARISON OF OBSERVED AND CALCULATED VALUES OF KRAFT PULP PROPERTIES

X_1	X_2	X_5	X_6	Yield, % on wood			Scr. Yield, % on wood			Kappa Number			Viscosity, cp		
				Obs.	Calc.[a]	Calc.[b]	Obs.	Calc.[a]	Calc.[b]	Obs.	Calc.[a]	Calc.[b]	Obs.	Calc.[a]	Calc.[b]
-1	-1	-1	-1	47.8	47.8	48.2	47.2	47.3	47.8	54.3	52.5	50.9	26.6	27.5	30.3
1	-1	-1	-1	42.7	43.0	42.6	42.7	42.9	42.5	21.2	21.6	22.2	15.9	15.1	14.3
-1	1	-1	-1	45.0	44.9	45.1	44.7	44.5	44.8	32.8	33.9	32.6	22.4	20.5	18.9
1	1	-1	-1	40.2	40.2	39.8	40.2	40.1	39.9	13.3	13.9	14.3	8.3	8.0	9.0
-1	-1	1	-1	45.9	46.1	46.6	45.7	45.6	46.2	29.8	31.8	33.5	31.8	27.5	30.1
1	-1	1	-1	42.2	41.3	41.1	42.2	41.2	41.1	15.8	16.0	14.6	15.5	15.1	14.2
-1	1	1	-1	44.3	43.2	43.7	43.9	42.8	43.5	21.1	20.5	21.9	18.6	20.5	19.1
1	1	1	-1	38.7	38.4	38.5	38.7	38.4	38.6	11.4	10.3	9.4	7.8	8.0	9.0
-1	-1	-1	1	53.4	52.0	51.4	52.8	51.6	50.9	94.5	94.3	--[d]	47.8	48.8	54.2
1	-1	-1	1	45.1	45.6	45.1	44.9	45.5	45.0	32.9	30.1	30.0	31.4	26.8	24.8
-1	1	-1	1	48.8	49.1	48.1	48.6	48.8	47.8	58.8	60.8	--[d]	35.4	36.3	34.2
1	1	-1	1	42.1	42.7	42.3	42.0	42.7	42.4	19.5	19.4	19.7	15.7	14.2	15.8
-1	-1	1	1	49.3	50.3	49.7	48.5	49.8	49.3	50.8	48.9	47.5	50.9	48.8	54.2
1	-1	1	1	44.0	43.8	43.6	44.0	43.8	43.6	20.9	19.1	19.9	27.3	26.8	24.8
-1	1	1	1	46.2	47.4	46.3	46.1	47.1	46.1	34.4	31.6	29.9	37.0	36.3	33.3
1	1	1	1	40.7	40.9	40.9	40.7	41.0	40.9	11.9	12.3	13.0	14.0	14.2	15.7
2	0	0	0	40.4	40.3	40.2	40.4	40.3	40.3	13.0	13.8	12.9	11.2	12.7	12.4
0	-2	0	0	46.7	46.5	47.0	46.6	46.4	46.8	34.4	33.7	36.7	28.2	33.8	34.3
0	2	0	0	41.5	40.7	41.3	41.5	40.8	41.3	15.0	14.0	15.6	12.9	13.3	13.7
0	0	-2	0	45.8	45.4	46.5	45.8	45.3	46.4	52.4	50.9	49.2	20.8	21.2	20.4
0	0	2	0	42.2	41.9	42.8	42.2	41.9	42.7	17.9	19.5	17.2	19.8	21.2	20.8
0	0	0	-2	41.7	42.6	--[c]	40.6	41.9	--[c]	15.6	14.8	14.6	9.3	9.7	9.6
0	0	0	2	50.4	49.4	--[c]	50.3	48.9	--[c]	29.6	31.9	29.0	28.2	30.6	31.8
0	0	0	0	43.7	43.6	43.6	43.6	43.6	43.5	20.6	21.8	22.4	20.3	21.2	20.3
0	0	0	0	42.3	43.6	43.6	42.2	43.6	43.5	20.9	21.8	22.4	19.8	21.2	20.3
0	0	0	0	44.7	43.6	43.8	44.7	43.6	43.7	21.8	21.8	22.9	22.9	21.2	20.8
0	0	0	0	43.3	43.6	43.7	43.3	43.6	43.6	21.5	21.8	22.4	20.4	21.2	20.4
0	0	0	0	43.8	43.6	43.7	43.8	43.6	43.6	21.8	21.8	22.4	23.4	21.2	20.4
0	0	0	0	43.5	43.6	43.7	43.5	43.6	43.6	22.2	21.8	22.5	19.6	21.2	20.4
0	0	0	0	42.8	43.6	43.7	42.8	43.6	43.6	20.0	21.8	22.6	24.1	21.2	20.5

[a]Calculated from polynomial model.
[b]Calculated from exponential model.
[c]The exponential yield models apply only for liquor-to-wood ratios in the range 3 to 5 (X_5 = -1 to +1).
[d]The exponential kappa number model applies only for kappa numbers less than 55.

charge, especially at short cooking times. It is also decreased by increasing the sulfidity and, again, the effect is more pronounced at short cooking times as well as at high liquor-to-wood ratio. Increasing the liquor-to-wood ratio increases the kappa number, especially at short cooking times and low sulfidities. Viscosity is decreased by increasing the effective alkali charge, especially at long cooking times. It is unaffected by sulfidity and is increased by increases in the liquor-to-wood ratio, especially at short cooking times. Again, it is emphasized that all of these statements concerning the effects of process variables on yield, kappa number, and viscosity apply at a fixed cooking time.

As mentioned before, the primary constraints on the degree to which the unbleached pulp lignin content can be reduced are pulp yield and pulp strength, as reflected in pulp viscosity. From this point of view, it is helpful to examine the effects of the pulping variables on yield and viscosity at constant lignin content, or kappa number, rather than at constant cooking time. These effects are shown graphically in Fig. 1-7.

Figures 1 and 2 show that, for a given kappa number, effective alkali charge has little or no effect on either viscosity or yield. Sulfidity, on the other hand, has a large effect on viscosity and a smaller one on yield, as shown in Fig. 3 and 4.

In general, increasing the liquor to wood ratio increases the viscosity at a given kappa number, as shown in Fig. 5. Figure 5 also gives an indication of how this comes about. Under the conditions shown, cooking for 60 minutes at a liquor-to-wood ratio of 3:1 gives a kappa number of 30 (Point A in the figure). If the liquor-to-wood ratio is increased from 3:1 to 4:1 while keeping all other cooking conditions constant, the kappa number increases to 38.5 and the viscosity increases to

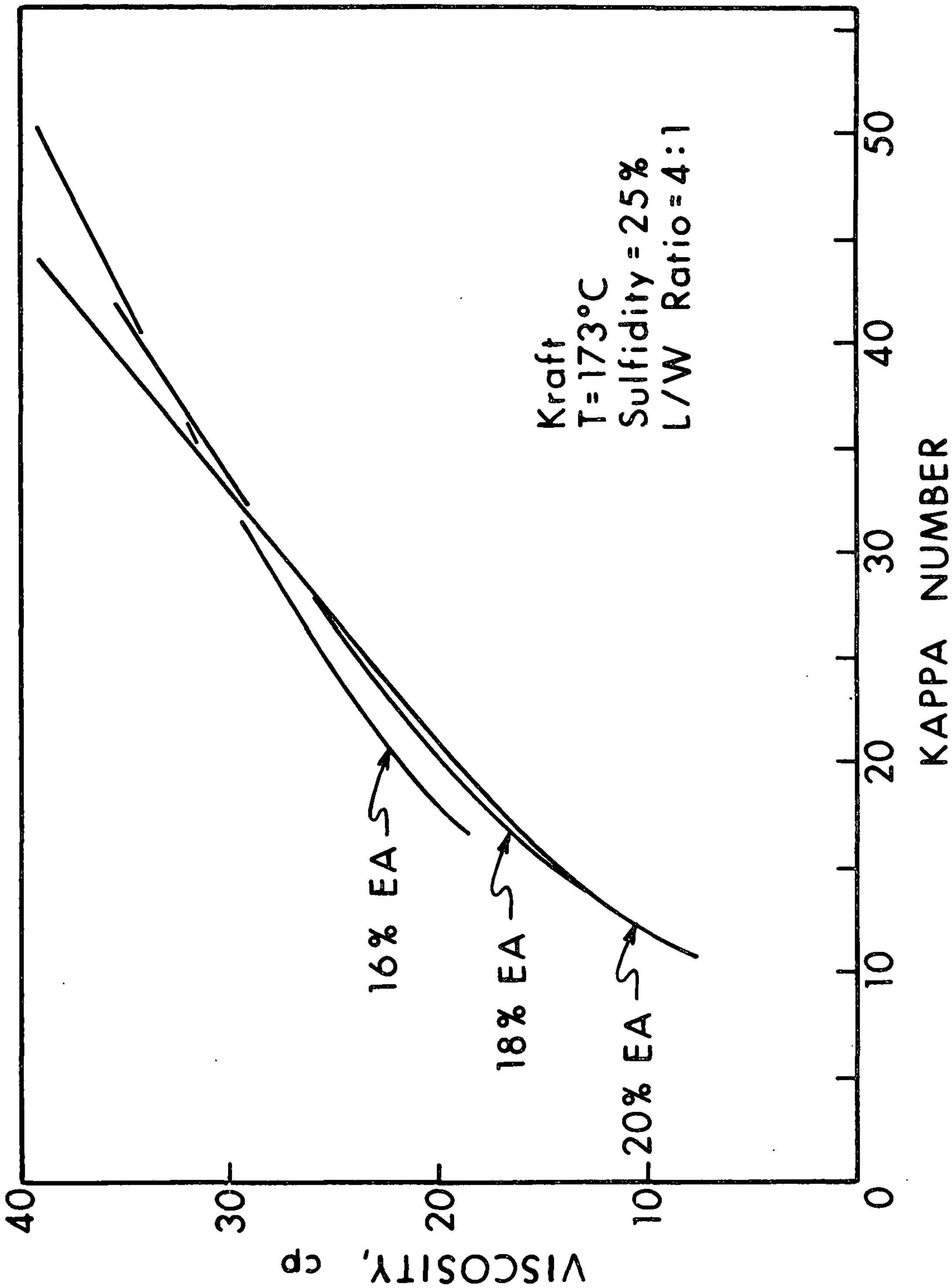

Figure 1. The Effect of Effective Alkali Charge on the Kraft Viscosity-Kappa Number Relationship

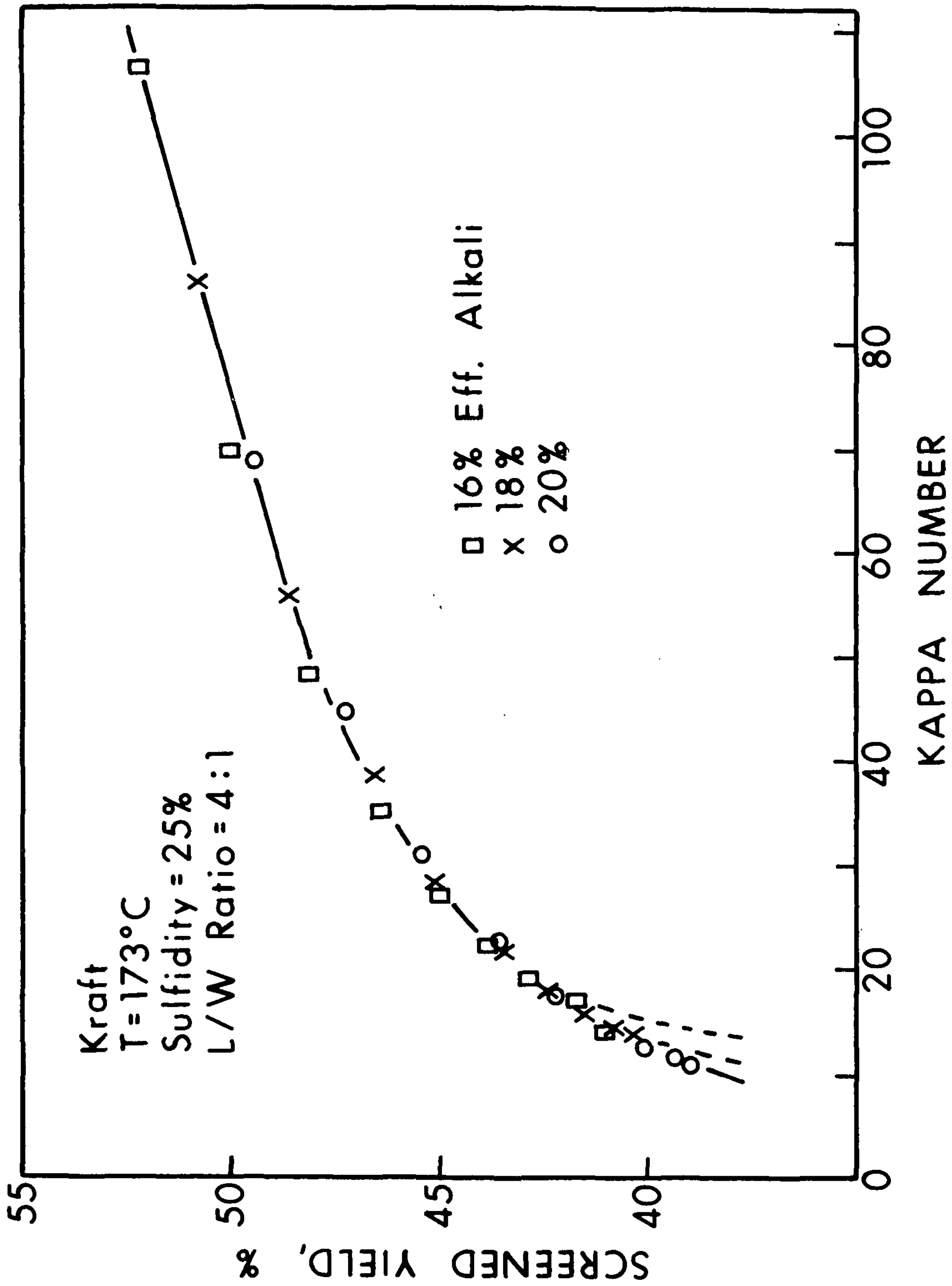

Figure 2. The Effect of Effective Alkali Charge on the Kraft Yield-Kappa Number Relationship

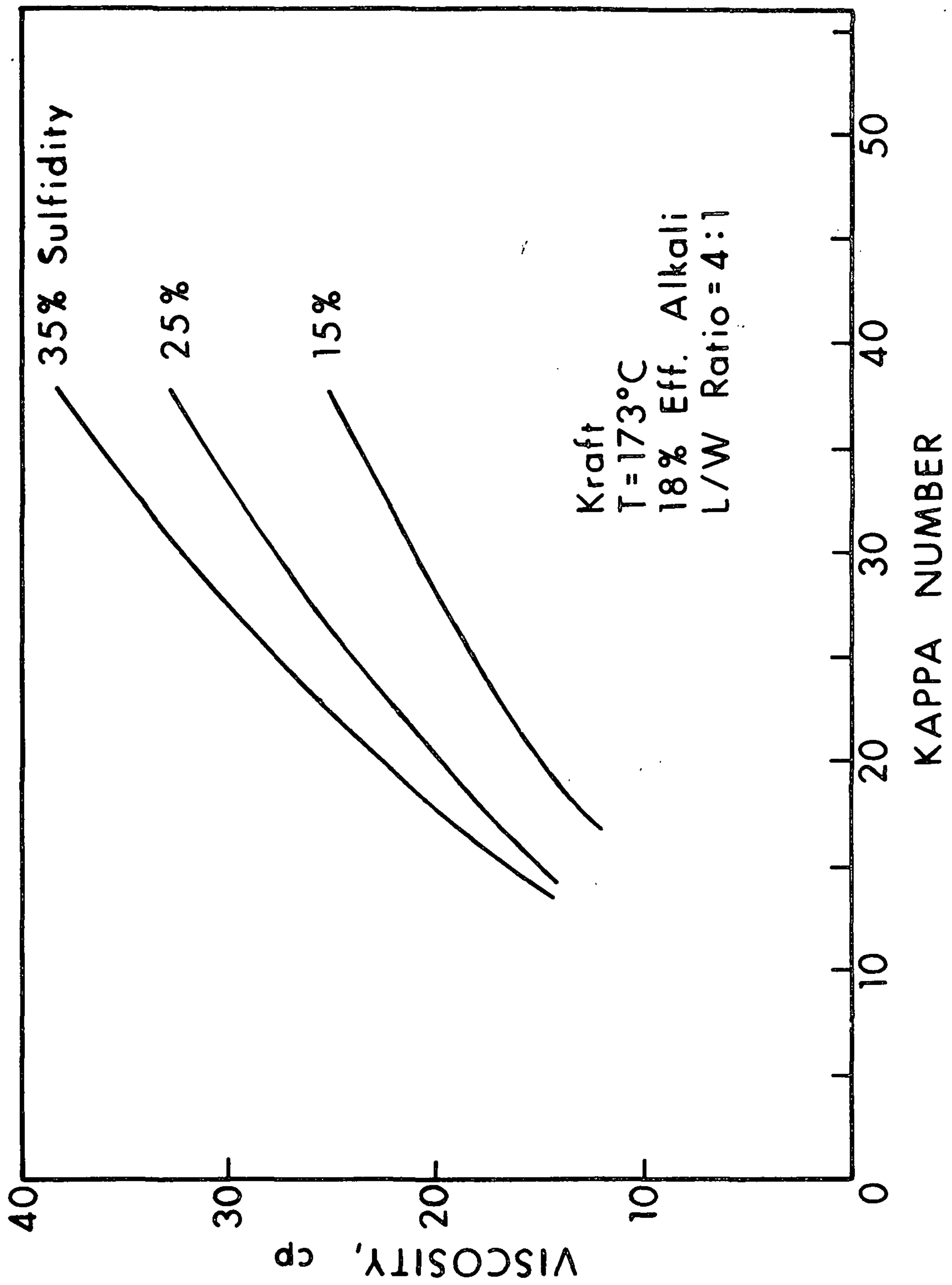

Figure 3. The Effect of Effective Sulfidity on the Kraft Viscosity-Kappa Number Relationship

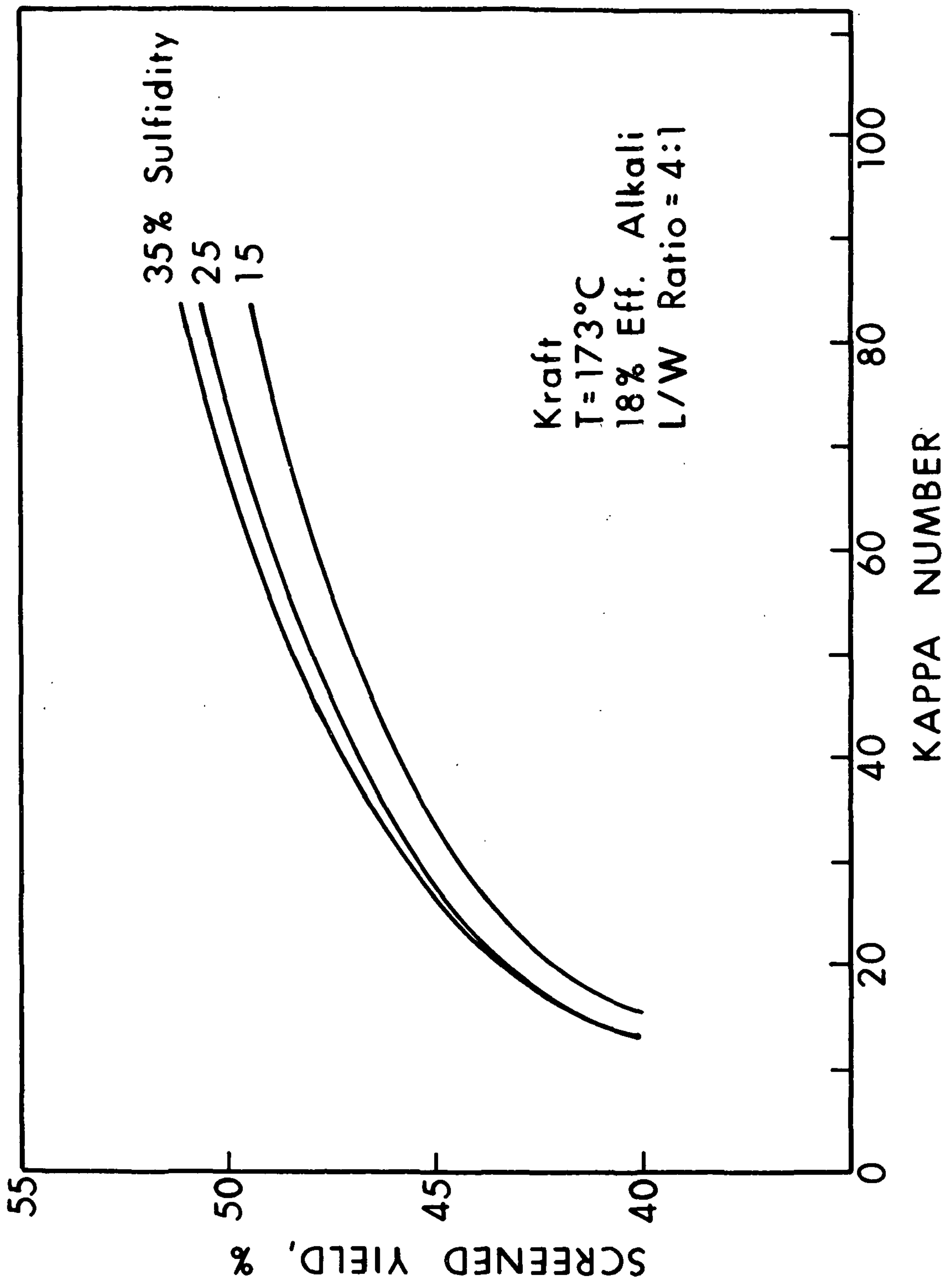

Figure 4. The Effect of Effective Sulfidity on the Kraft Yield-Kappa Number Relationship

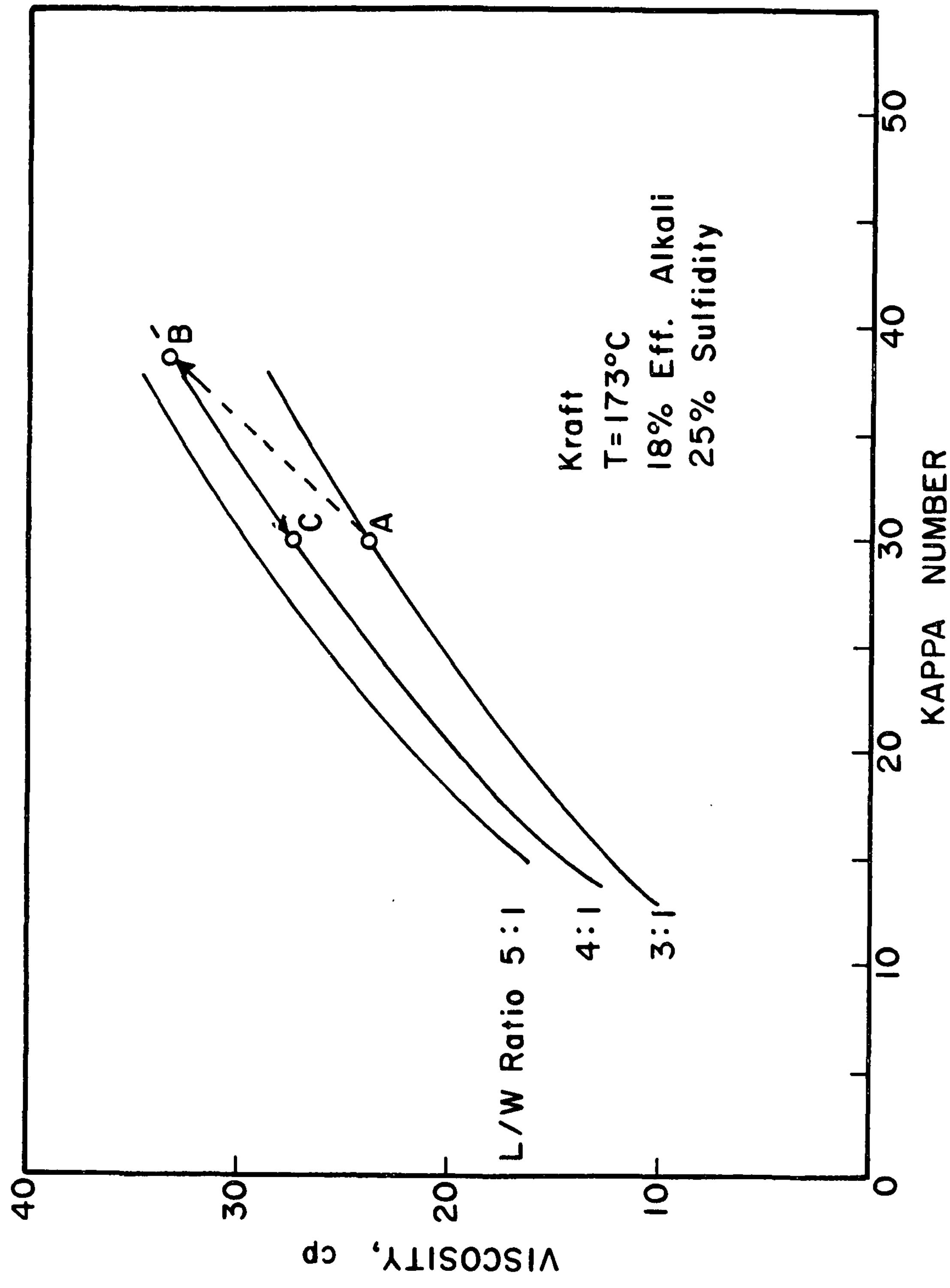

Figure 5. The Effect of Effective Liquor-to-Wood Ratio on the Kraft Viscosity-Kappa Number Relationship

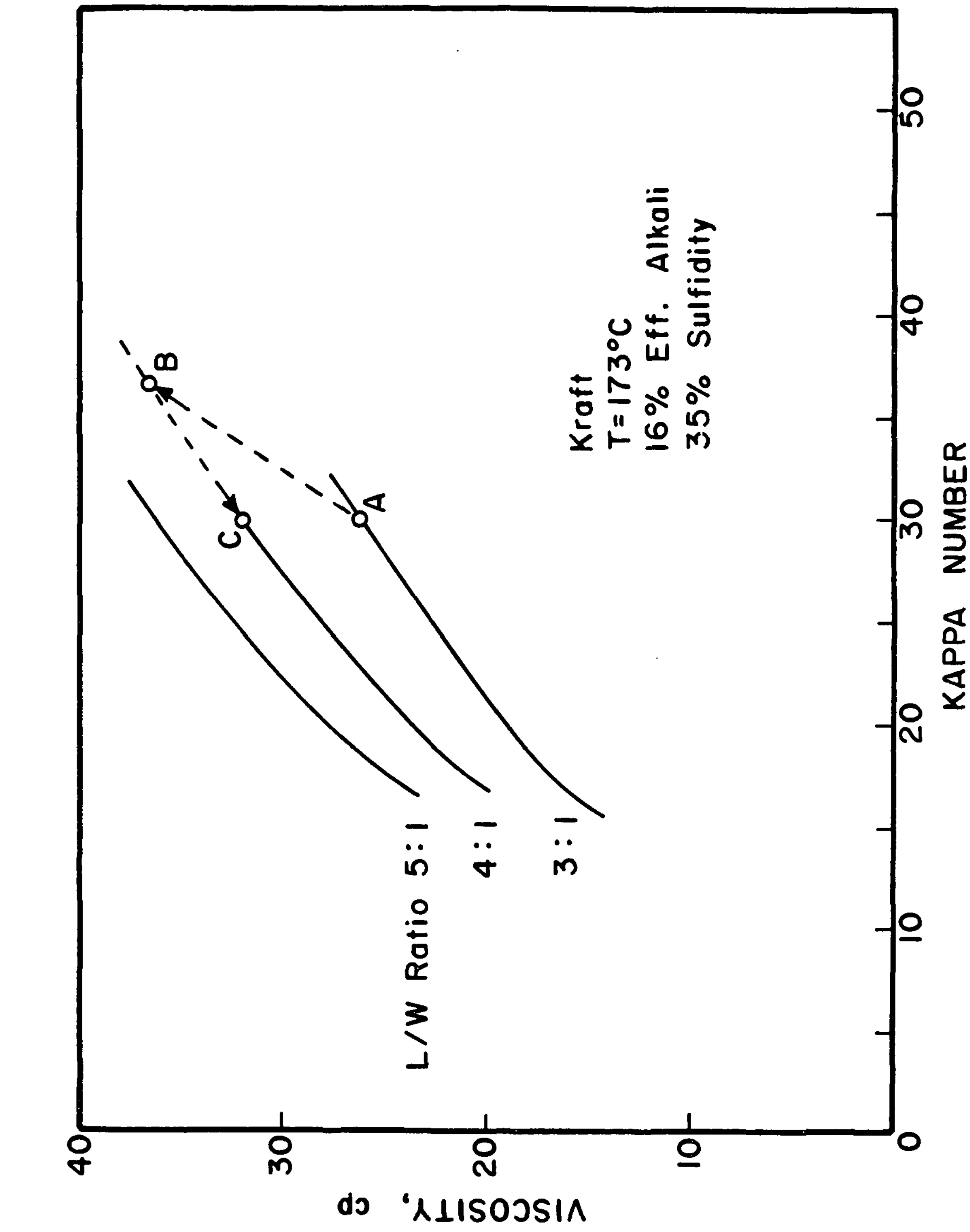

Figure 6. The Effect of Effective Liquor-to-Wood Ratio on the Kraft Viscosity-Kappa Number Relationship

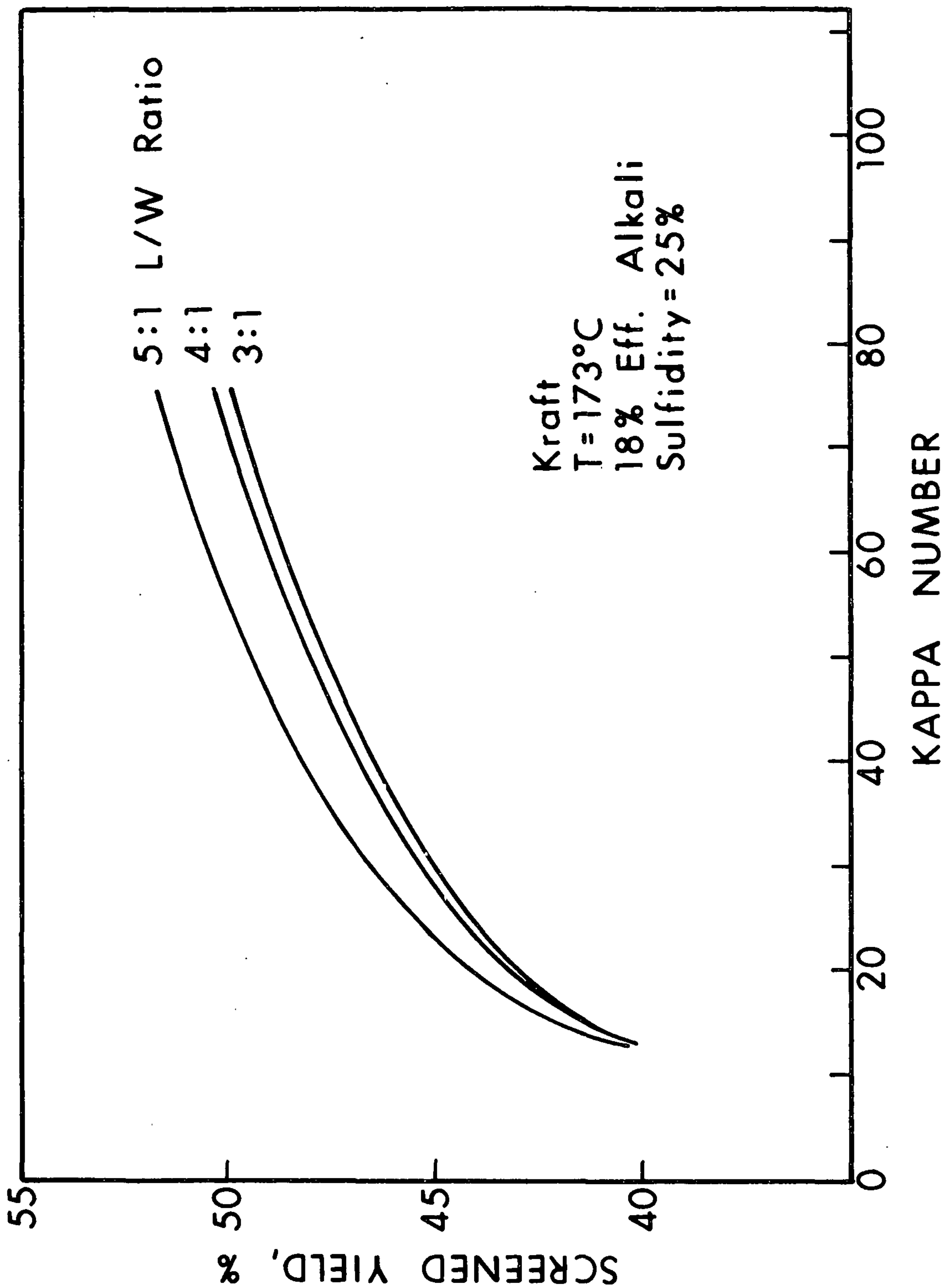

Figure 7. The Effect of Effective Liquor-to-Wood Ratio on the Kraft Yield-Kappa Number Relationship

33.1 (Point B in the figure). To restore the kappa number to its original value of 30 it is now necessary to increase the cooking time from 60 minutes to 84 minutes. When this is done, the viscosity is reduced only from 33.1 to 27.5 (Point C in the figure). The net result is an increase in viscosity from 23.6 to 27.5 when the liquor-to-wood ratio is increased from 3:1 to 4:1 at a kappa number of 30.

In general, the effect of a change in any one process variable on the position of the viscosity-kappa number relationship is not independent of the levels of the remaining pulping variables. That this is true for the effect of liquor-to-wood ratio is apparent from Fig. 6. This figure shows viscosity kappa number relationships for a lower effective alkali and higher sulfidity than those shown in Fig. 5. Under these conditions and at a liquor-to-wood ratio of 3:1, it is necessary to cook for 64 minutes to reach the target kappa number of 30. At this kappa number the pulp has a viscosity of 26.2. Increasing the liquor to wood ratio to 4:1 while maintaining all other conditions constant increases the kappa number to 36.7 and the viscosity to 36.8. The kappa number is restored to its original value of 30 by an increase in cooking time to 88 minutes, which also reduces the viscosity to 32.0. The net effect is an increase in the viscosity from 26.2 to 32.0 when the liquor-to-wood ratio is increased from 3:1 to 4:1 at a kappa number of 30. This positive effect of 5.8 viscosity units may be compared to the corresponding effect of 3.9 units on Fig. 5. It is apparent that the beneficial effect of increasing the liquor-to-wood ratio is greater when the liquor is lower in effective alkali and higher in sulfidity. The reason is that the effect of liquor-to-wood ratio on viscosity is independent of effective alkali, sulfidity, and cooking time, but the effect on kappa number depends on cooking time and sulfidity, as shown by the presence of X_1X_6 and X_5X_6 interaction terms in the equation for kappa number.

As shown in Fig. 7, there is a beneficial effect of liquor-to-wood ratio on the yield-kappa number relationship, but only at higher liquor-to-wood ratio.

Optimization

To produce unbleached pulp with the lowest possible lignin content, the best pulping conditions are those which give the lowest possible kappa number while maintaining pulp strength and yield at acceptable levels. In optimization terms, the best conditions are those which minimize the kappa number function subject to constraints on viscosity and yield. The problem of finding these conditions can be simplified by initially omitting the yield constraint from consideration. This is permissible since changes in process variables which tend to increase the viscosity generally also tend to increase the yield, and small yield losses will probably be more tolerable than pulp strength losses.

Kappa number minimizing conditions were found using the constrained direct search algorithm of Luus and Jakkola (9). A computer program based on this algorithm was written and used with the equations of Table I to find the desired process conditions, subject to a constraint on the pulp viscosity. The level of the viscosity constraint was varied to obtain the minimum kappa number and its associated process conditions as a function of viscosity. The effect of imposing additional constraints in the form of upper limits on cooking time and liquor-to-wood ratio was also investigated. The results are contained in Table V, together with data representing a conventional kraft process in which the kappa number is varied by extending the cooking time with liquor of fixed initial composition. Terminating a conventional kraft cook when the pulp viscosity reaches 30 results in a kappa number of 32. It is possible to reduce the kappa number to 18 simply by extending the cook, but it is necessary to nearly double the cooking time and significant

TABLE V

KRAFT OPTIMIZATION RESULTS

Process Conditions[a] for Minimizing Kappa Number at Various Viscosity Levels Compared to Conventional Conditions

Secondary Constraint	Viscosity Constraint, cp (Lower Limit)	Predictions: Kappa Number	Predictions: Yield, %	Predictions: Carbohydrate Yield, %	Process Conditions: Time at 173°C, min	Process Conditions: Effective Alkali, %	Process Conditions: Sulfidity, %	Process Conditions: Liquor-to-wood Ratio
None	15	12.8	41.2	40.4	189	19.4	35.2	5.1
	20	15.3	42.4	41.4	201	17.4	34.4	5.1
	25	18.0	43.6	42.4	188	16.4	34.3	5.1
	30	21.4	44.8	43.4	170	15.5	33.1	5.0
	35	26.6	46.4	44.5	138	15.1	33.9	5.0
H ≤ 3000	15	13.0	40.8	40.0	139	21.0	36.5	4.6
	20	16.1	43.0	42.0	140	19.5	39.2	5.1
	25	19.3	44.6	43.3	140	18.1	39.2	5.3
	30	22.6	45.6	44.0	140	16.6	38.2	5.3
	35	26.6	46.4	44.5	140	15.1	33.9	5.0
H ≤ 2000	15	15.0	41.2	40.3	89	21.1	33.0	3.2
	20	17.1	42.1	41.0	89	21.1	36.6	4.1
	25	20.4	43.9	42.6	89	20.4	38.4	4.7
	30	24.5	45.7	44.0	88	19.2	39.9	5.0
	35	29.2	47.1	45.0	89	17.9	40.1	5.2
L/W ≤ 4.0	15	13.4	40.4	39.6	117	21.2	36.7	4.0
	20	16.6	41.5	40.5	205	16.0	34.4	4.0
	25	19.7	42.9	41.6	180	14.9	33.1	4.0
	30	25.9	44.7	43.0	55	20.1	37.7	4.0
	35	31.2	45.8	43.6	42	19.7	37.6	4.0
Conventional kraft	20	17.6	42.2	41.1	210	16.0	25.0	4.0
	25	25.3	44.4	42.7	135	16.0	25.0	4.0
	30	32.2	46.2	44.0	99	16.0	25.0	4.0
	35	41.1	47.6	44.7	74	16.0	25.0	4.0

[a]Constant conditions: Maximum temperature 173°.
Time to maximum temperature 90 minutes.

losses in viscosity and yield are incurred. Optimization subject to the requirement that the pulp viscosity be no lower than 30, but with no other constraints, gives process conditions which are predicted to result in a kappa number of only 21. Relative to the conventional kraft case, the carbohydrate yield is only marginally lower, and the necessary pulping conditions involve increases in cooking time, sulfidity, and liquor-to-wood ratio. As the viscosity requirement is progressively relaxed, lower and lower kappa numbers are achievable, the optimized conditions changing principally with respect to cooking time and effective alkali charge, both of which increase. Imposing an additional constraint, in the form of a maximum allowable cooking time (or H-factor, since the temperature is constant), increases the minimum kappa number achievable at any given viscosity level. When the H-factor constraint is set at 2000 (89 minutes at 173°C), the minimum kappa number at 30 viscosity rises from 21.4 to 24.5. If the additional constraint is in the form of an upper limit of 4.0 on the liquor-to-wood ratio, the minimum kappa number achievable at the same viscosity level is 25.9. The effect of constraining the liquor-to-wood ratio becomes less as the viscosity requirement is relaxed.

Relationships between the minimum achievable kappa number and the corresponding viscosity constraint may be thought of as optimized viscosity-kappa number relationships. The various points on such a curve are arrived at by holding the cooking time constant and varying the initial liquor composition. Two such curves for different H factors are shown in Fig. 8. Also included in the figure for comparison is the viscosity-kappa number relationship for a conventional kraft cook in which the cooking time is varied for constant initial liquor composition. It is apparent that substantial reductions in kappa number at normal viscosity levels can be achieved by judicious variations in the amount and composition of cooking liquor.

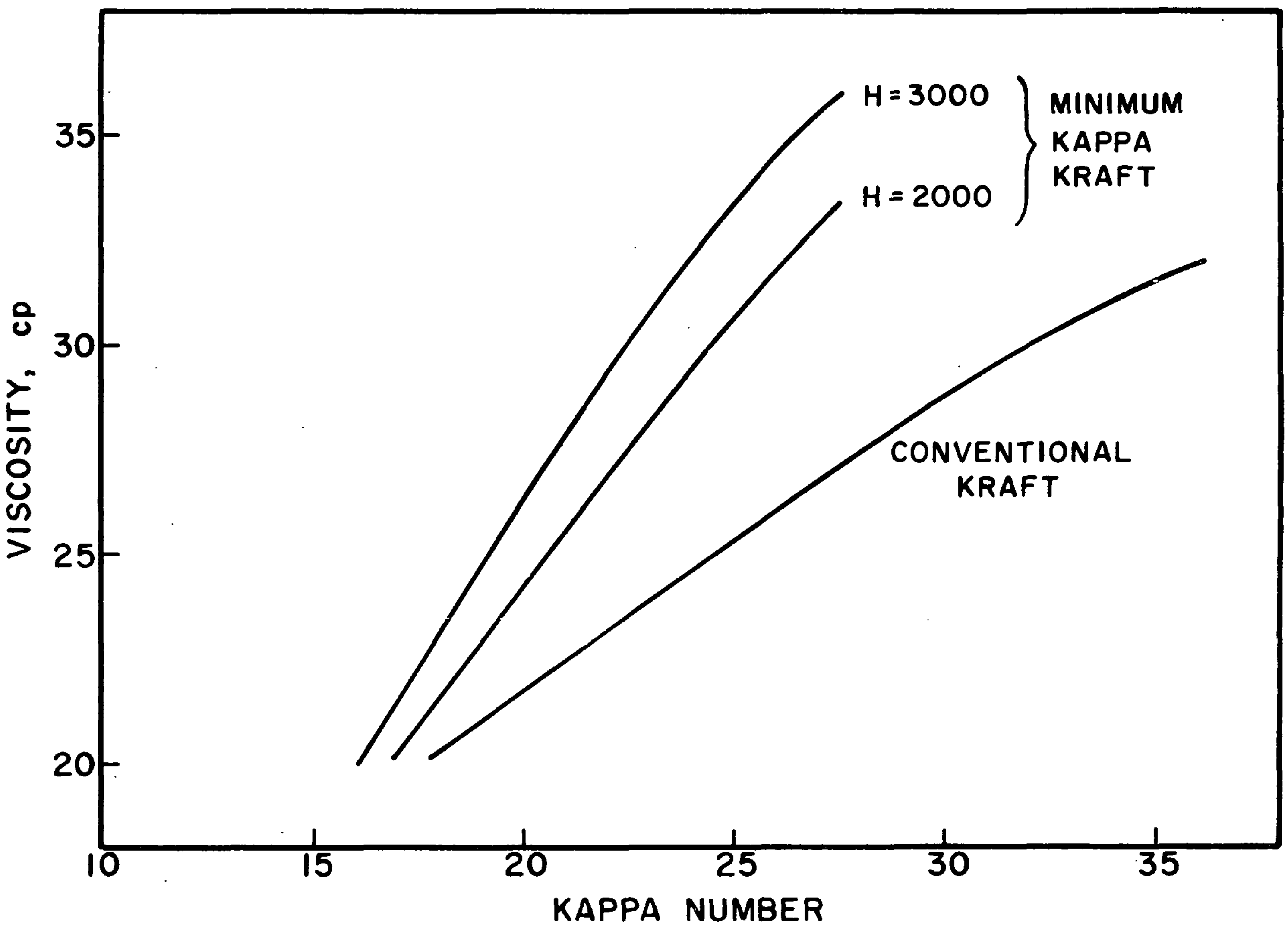

Figure 8. Optimized and Conventional Kraft Viscosity-Kappa Number Relationships. In the Conventional Case, Kappa Number was Varied by Varying Cooking Time. The Optimized Pulping Procedure Involves Holding the Cooking Time Constant at Values Corresponding to the H-Factor Values Shown and Varying the Liquor-to-Wood Ratio and Liquor Composition

The validity of the assumption that using viscosity as the primary constraint would result in conditions that give satisfactory yield levels is borne out by the data shown in Fig. 9. Use of the kappa number minimizing conditions may be expected to allow substantial reductions in kappa number with no loss in yield.

KRAFT-ANTHRAQUINONE PULPING

Because anthraquinone was known to have a beneficial effect on the selectivity of alkaline delignification, it was of interest to examine its use in the context of low-lignin pulping. For this purpose a procedure almost identical to that described above for kraft pulping was employed. The only exception was that liquor-to-wood ratio was replaced as a variable in the experiments by anthraquinone charge.

Pulping Models

The pulping data obtained are collected in Table VI and the regression equations of the polynomial and exponential model in Tables VII and VIII, respectively. Once again, all of the equations were found to provide a satisfactory description of the experimental data. This may be inferred from the comparison of observed and calculated values in Table IX.

The effects of the individual independent variables can be assessed by examining the regression equations. Yield decreased rapidly at low values and more slowly at high values of cooking time, effective alkali charge, and sulfidity. The effect of anthraquinone charge on yield was negative at low values of effective alkali and positive at high values. The negative effect of anthraquinone on yield was due to its negative effect on the lignin content of the unbleached pulp at fixed values of the other variables. Kappa number, like yield, decreased rapidly at low values and more slowly at high values of cooking time, effective alkali charge, and

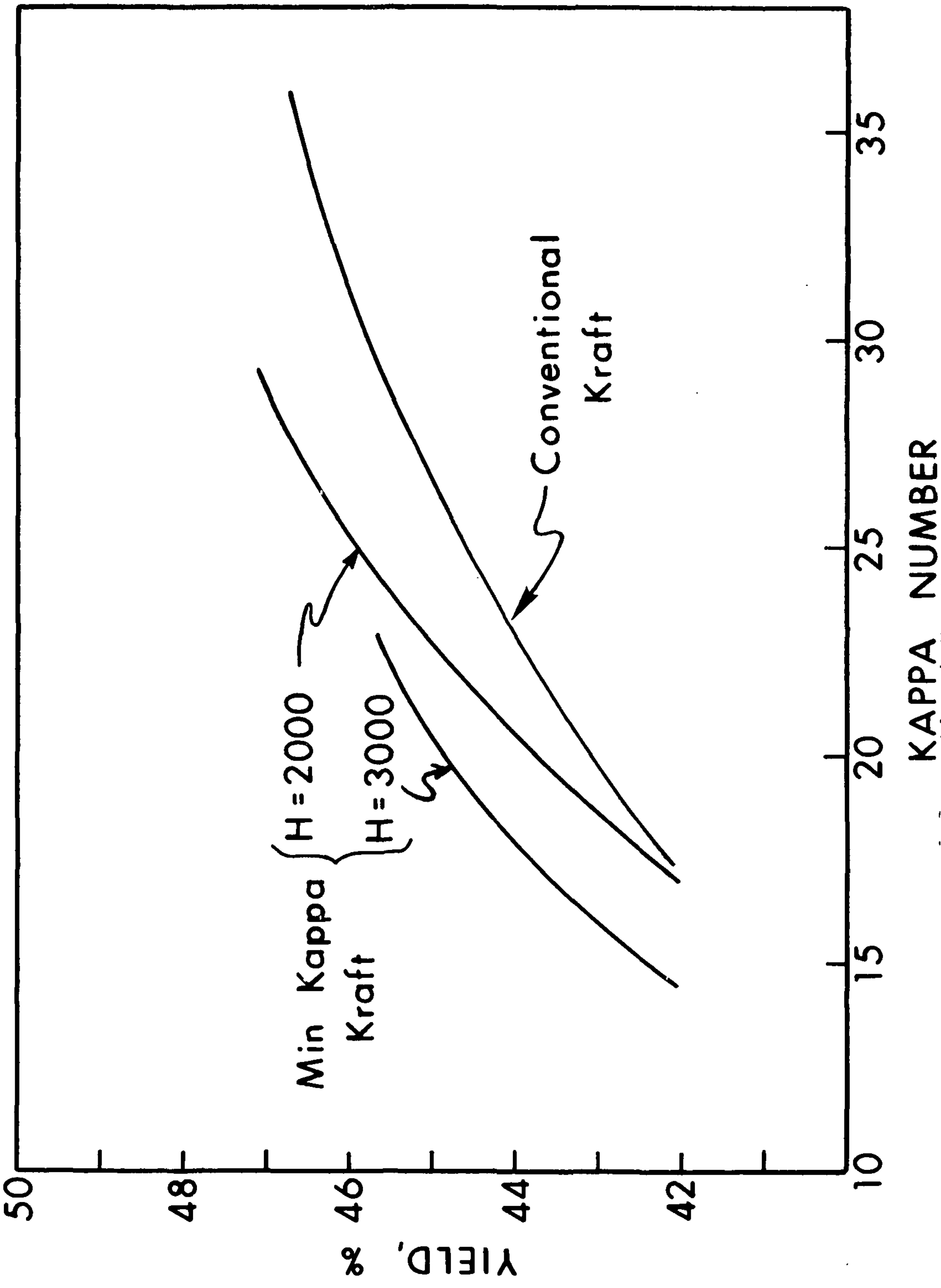

Figure 9. Optimized and Conventional Kraft Yield-Kappa Number Relationships. In the Conventional Case, Kappa Number was Varied by Varying Cooking Time. The Optimized Pulping Procedure Involves Holding the Cooking Time Constant at Values Corresponding to the H-Factor Values Shown and Varying the Liquor-to-Wood Ratio and Liquor Composition

TABLE VI

KRAFT-ANTHRAQUINONE PULPING DATA

Cook No.	Time at 173°, min	H-Factor	Effective Alkali, %	Anthraquinone, %	Sulfidity, %	Yield, %	Screened Yield, %	Kappa No.	Viscosity, cp
26.6	60	1457	16	0.05	15	51.6	51.3	55.8	35.6
30.3	180	3826	16	0.05	15	45.6	45.5	21.0	21.6
26.2	60	1457	20	0.05	15	46.8	46.8	31.8	26.4
26.1	180	3817	20	0.05	15	42.4	42.4	14.0	15.9
27.5	60	1469	16	0.20	15	49.4	49.2	36.9	36.7
26.3	180	3817	16	0.20	15	46.2	46.2	18.2	22.7
28.7	60	1449	20	0.20	15	47.4	47.3	30.1	32.7
26.5	180	3817	20	0.20	15	43.2	43.2	12.8	13.4
28.2	60	1449	16	0.05	35	49.0	48.6	36.5	48.8
29.6	180	3770	16	0.05	35	44.8	44.7	17.1	26.5
29.5	60	1433	20	0.05	35	45.5	45.5	20.8	26.5
30.4	180	3826	20	0.05	35	41.8	41.8	10.2	12.7
26.4	60	1457	16	0.20	35	49.0	48.8	27.5	38.9
27.6	180	3831	16	0.20	35	44.2	44.1	14.8	37.5
28.5	60	1449	20	0.20	35	47.0	46.9	20.7	30.8
28.1	180	3788	20	0.20	35	42.2	42.2	11.0	12.7
28.4	240	4993	18	0.10	25	42.3	42.3	11.8	13.8
27.4	120	2626	14	0.10	25	48.7	48.2	29.9	33.4
27.1	120	2626	22	0.10	25	42.3	42.0	12.3	12.3
30.6	120	2646	18	0.025	25	45.0	45.0	19.2	23.9
29.3	120	2613	18	0.400	25	45.7	45.7	14.4	22.4
27.2	120	2626	18	0.10	5	47.0	47.0	25.5	20.8
29.4	120	2613	18	0.10	45	44.1	44.1	15.1	24.2
26.7	120	2637	18	0.10	25	45.1	45.1	18.6	25.4
27.3	120	2626	18	0.10	25	44.6	44.6	17.1	19.2
28.3	120	2631	18	0.10	25	44.9	44.8	17.2	23.8
29.1	120	2613	18	0.10	25	45.3	45.3	16.7	20.9
29.2	120	2613	18	0.10	25	44.7	44.7	16.6	24.6
30.1	120	2646	18	0.10	25	44.8	44.8	17.9	22.6
30.5	120	2646	18	0.10	25	44.7	44.6	17.1	23.2

TABLE VII

POLYNOMIAL MODEL FOR KRAFT-ANTHRAQUINONE PULPING OF LOBLOLLY PINE[a,b,c]

	R^2	Coefficient of Variation of Measured Quantity, %: Residual[d]	Coefficient of Variation of Measured Quantity, %: Replicates[e]
Total yield, % = $45.0 - 2.2X_1 - 1.5X_2 - 0.6X_5 + 0.3X_2X_3 + 0.5X_1^2 + 0.2X_2^2 + 0.2X_5^2$	0.97	1.0	0.6
Screened yield, % = $45.0 - 2.2X_1 - 1.4X_2 - 0.6X_5 + 0.3X_2X_3 + 0.5X_1^2 + 0.2X_5^2$	0.97	1.0	0.6
ln (Kappa no.) = $2.85 - 0.39X_1 - 0.21X_2 - 0.07X_3 + 0.14X_5 + 0.03X_1X_3 + 0.04X_1X_5 + 0.06X_2X_3 + 0.11X_1^2 + 0.03X_2^2 + 0.04X_5^2$	0.99	5.2	4.0
ln (Viscosity, cp) = $3.18 - 0.29X_1 - 0.25X_2 - 0.09X_1X_2$	0.89	13	9.8

[a]The independent variables in the above equations are defined as follows:

$$X_1 = \frac{(\text{Time at } 173°\text{C, min}) - 120}{60}$$

$$X_2 = \frac{(\text{Effective alkali}) - 18}{2}$$

$$X_3 = \frac{\log\ (\text{AQ charge}) + 1}{\log\ 2}$$

$$X_5 = \frac{(\text{Sulfidity}) - 25}{10}$$

[b]The equations are valid only within the region bounded by $X_1^2 + X_2^2 + X_3^2 + X_5^2 = 4$.
[c]Constant conditions: 90-minute rise to a maximum temperature of 173°C, liquor-to-wood ratio 4.0.
[d]Calculated from sum of squared deviations of all data points from the fitted surface.
[e]Calculated from variance of replicate center points.

TABLE VIII

EXPONENTIAL MODEL FOR KRAFT-AQ PULPING OF LOBLOLLY PINE

	R^2	Coefficient of Variation of Measured Quantity, %: Calculated from Residual Mean Square	Coefficient of Variation of Measured Quantity, %: Calculated from Replicate Measurements
Total yield, %[a] $= \dfrac{239.8\ L/W^{0.0054}}{EA^{0.2830}S^{0.0263}H^{0.0960}}$	0.97	0.8	0.6
Screened yield, %[a] $= \dfrac{227.5\ 1/W^{0.0055}}{EA^{0.2709}S^{0.0270}H^{0.0937}}$	0.97	0.8	0.6
Kappa no.[b] $= \dfrac{2.252 \times 10^6}{EA^{1.7603}AQ^{0.0780}S^{0.2783}H^{0.7537}}$	0.96	7.8	4.0
Viscosity[c] $= \dfrac{1.491 \times 10^6}{EA^{1.9806}H^{0.6840}}$	0.91	11.2	9.7

[a]The exponential yield equations apply only for yields less than 50%.
[b]The exponential kappa number equation applies only for kappa numbers less than 50.
[c]An apparently spurious data point was omitted in deriving the viscosity equation; see Table IX.

TABLE IX

COMPARISON OF OBSERVED AND CALCULATED VALUES OF KRAFT-AQ PULP PROPERTIES

				Yield, % on wood			Scr. Yield, % on wood			Kappa Number			Viscosity, cp		
X_1	X_2	X_5	X_6	Obs.	Calc.[a]	Calc.[b]	Obs.	Calc.[a]	Calc.[b]	Obs.	Calc.[a]	Calc.[b]	Obs.	Calc.[a]	Calc.[b]
-1	-1	-1	-1	51.6	50.6	--[c]	51.3	50.4	--[c]	55.8	52.9	--[d]	35.6	34.3	42.1
1	-1	-1	-1	45.6	46.1	45.4	45.5	46.0	45.3	21.0	21.3	20.3	21.6	23.0	21.8
-1	1	-1	-1	46.8	46.9	46.7	46.8	46.9	46.7	31.8	31.2	28.3	29.8	27.1	18.9
1	1	-1	-1	42.4	42.4	42.6	42.4	42.4	42.6	14.0	12.6	13.7	15.9	14.1	14.0
-1	-1	1	-1	49.4	50.0	50.1	49.2	49.8	49.9	36.9	39.0	37.4	36.7	34.3	41.9
1	-1	1	-1	46.2	45.4	45.7	46.2	45.3	45.6	18.2	17.5	18.2	22.7	23.0	21.8
-1	1	1	-1	47.4	47.6	47.1	47.3	47.5	47.1	30.1	28.9	25.5	32.7	29.8	27.2
1	1	1	-1	43.2	43.1	42.9	43.2	43.1	43.0	12.8	13.0	12.3	13.4	14.1	14.0
-1	-1	-1	1	49.0	49.4	48.7	48.6	49.1	48.5	36.5	36.7	33.3	48.8	41.0	42.3
1	-1	-1	1	44.8	44.9	44.4	44.7	44.7	44.3	17.1	17.3	16.2	26.5	27.4	22.0
-1	1	-1	1	45.5	45.7	45.5	45.6	45.7	20.8	21.6	22.7	26.5	25.0	27.4	34.2
1	1	-1	1	41.8	41.2	41.7	41.8	41.2	41.7	10.2	10.2	10.8	12.7	11.8	14.0
-1	-1	1	1	49.0	48.7	49.1	48.8	48.5	27.5	27.0	29.8	38.9	41.0	42.1	54.2
1	-1	1	1	44.2	44.2	44.7	44.1	44.1	44.6	14.8	14.2	14.4	37.5[e]	27.4	21.8[e]
-1	1	1	1	47.0	46.4	46.1	46.9	46.2	46.0	20.7	20.0	20.2	30.8	25.0	27.2
1	1	1	1	42.2	41.9	42.0	42.2	41.8	42.0	11.0	10.5	9.8	12.7	11.8	14.1
2	0	0	0	42.3	42.7	42.4	42.3	42.8	42.4	11.8	12.6	11.1	13.8	13.5	14.4
0	-2	0	0	48.7	48.7	48.4	48.2	48.0	48.2	29.9	29.9	28.0	33.4	3927	36.7
0	2	0	0	42.3	42.7	42.6	42.0	42.2	42.6	12.3	13.1	12.6	12.3	14.7	15.0
0	0	-2	0	45.0	45.0	44.6	45.0	45.1	44.6	19.2	19.8	20.3	23.9	24.0	22.2
0	0	2	0	45.7	45.0	45.4	45.7	45.1	45.4	14.4	15.1	16.2	22.4	24.0	22.4
0	0	0	-2	47.0	47.0	47.0	47.0	47.0	25.5	27.0	28.2	20.8	24.0	22.3	9.6
0	0	0	2	44.1	44.5	44.4	44.1	44.5	44.3	15.1	15.2	15.3	24.2	24.0	22.4
0	0	0	0	45.1	45.0	45.0	45.1	45.1	45.0	18.6	17.3	17.9	25.4	24.0	22.2
0	0	0	0	44.6	45.0	45.1	44.6	45.1	45.0	17.1	17.3	18.0	19.2	24.0	22.3
0	0	0	0	44.9	45.0	45.1	44.8	45.1	45.0	17.2	17.3	18.0	23.8	24.0	22.3
0	0	0	0	45.3	45.0	45.1	45.3	45.1	45.0	16.7	17.3	18.1	20.9	24.0	22.4
0	0	0	0	44.7	45.0	44571	44.7	45.1	45.0	16.6	17.3	18.1	24.6	24.0	22.4
0	0	0	0	44.8	45.0	45.0	44.8	45.1	45.0	17.9	17.3	17.9	22.6	24.0	22.2
0	0	0	0	44.7	45.0	45.0	44.6	45.1	45.0	17.1	17.3	17.9	23.2	24.0	22.2

[a]Calculated from polynomial model.
[b]Calculated from exponential model.
[c]The exponential yield equations apply only for yields less than 50%.
[d]The exponential kappa number equation applies only for kappa numbers less than 50.
[e]Data point omitted in deriving exponential viscosity equation.

sulfidity. The effect of effective alkali was greater at lower anthraquinone charges, and the effect of sulfidity was greater at short cooking times. The effect of anthraquinone was greatest at short cooking times and low effective alkali charges. It is interesting to note that the accelerating effect of anthraquinone disappeared entirely at high effective alkali charges and very long cooking times.

Viscosity decreased with increasing cooking time and effective alkali charge but was independent of anthraquinone charge. The decrease in viscosity associated with increases in effective alkali charge was greatest at long cooking times and high sulfidities. Under these conditions it was a very large effect. The independence of anthraquinone charge and viscosity and the negative effect of effective alkali on viscosity were also noted by Kubes _et al._ (_10_) after the present work was done.

Evaluation of the effects of the independent variables on viscosity at constant kappa number gave the results shown in Fig. 10 through 15. It is apparent from Fig. 10 and 11 that increasing the effective alkali charge decreased the viscosity at a given kappa number but had no effect on the yield. Increasing the sulfidity increased the viscosity at fixed kappa but, like effective alkali, it did not affect the yield when the comparison was made under these conditions. This is apparent from Fig. 12 and 13. Figures 14 and 15 show that anthraquinone has a beneficial effect on both viscosity and yield at a given kappa number. The yield improvement at constant kappa number was observed in spite of the absence of any direct effect of anthraquinone on pulp yield. It is a consequence of the reduction in cooking time which addition of anthraquinone allows.

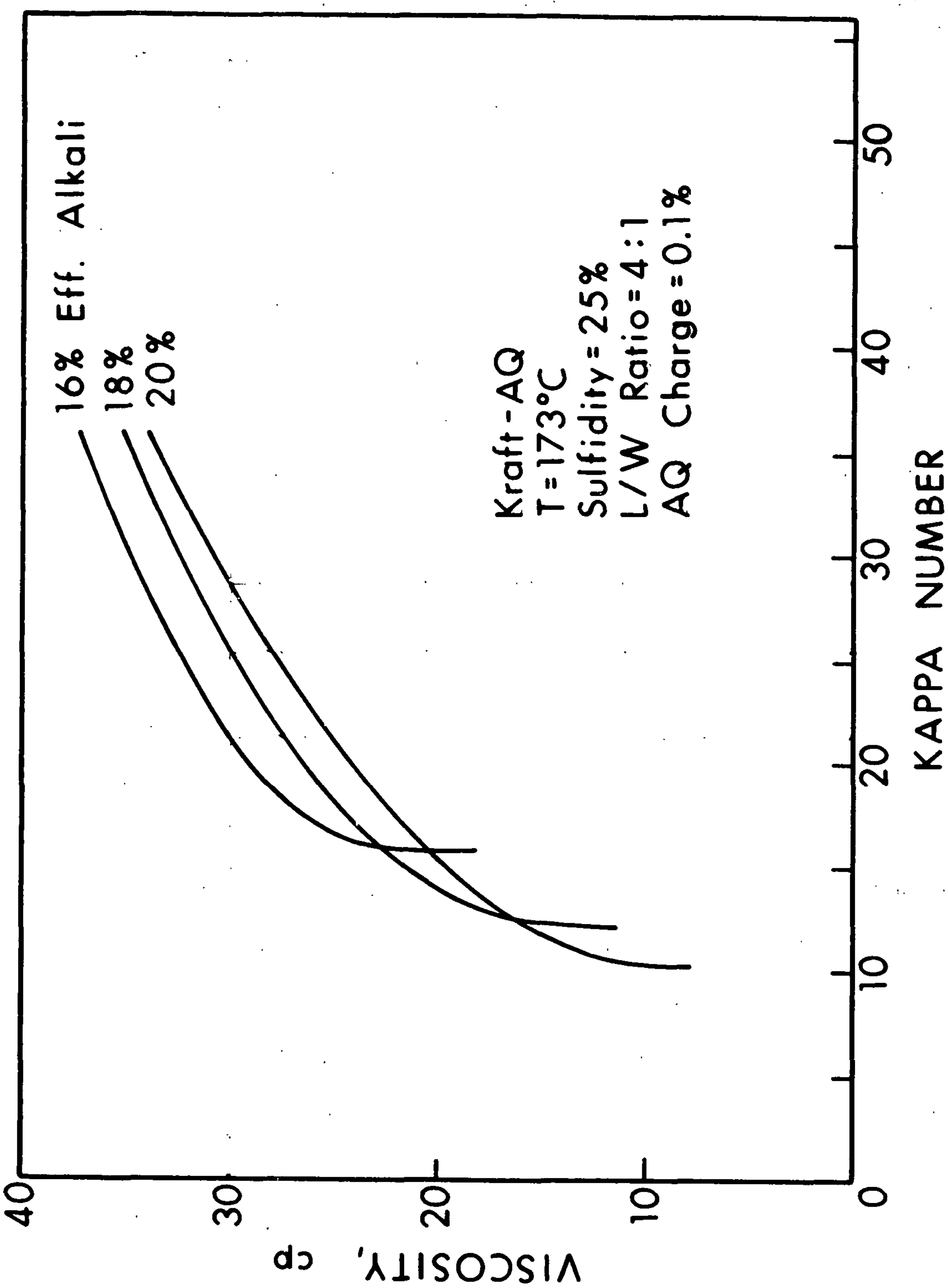

Figure 10. The Effect of Effective Alkali on the Kraft-AQ Viscosity-Kappa Number Relationship

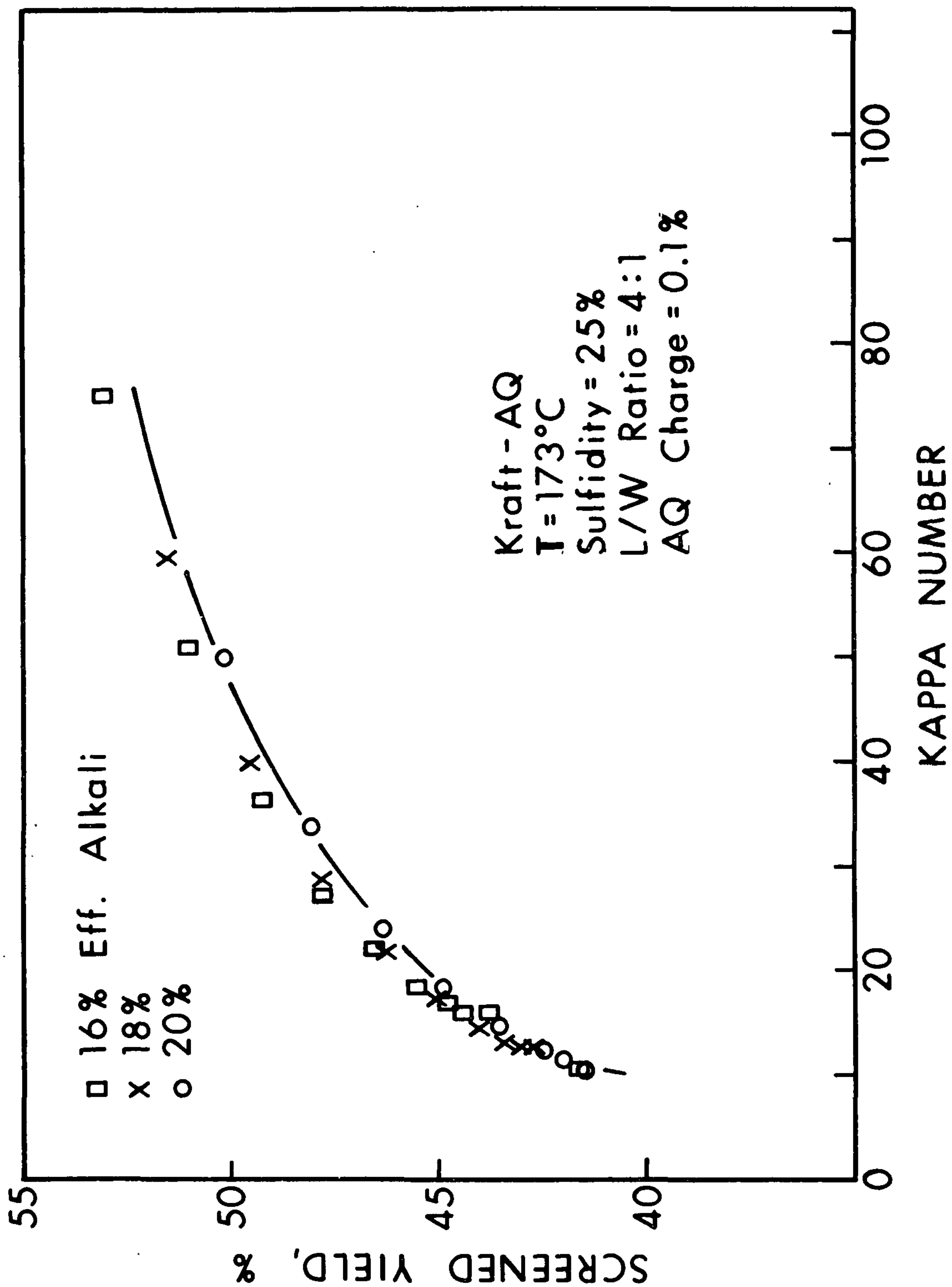

Figure 11. The Effect of Effective Alkali on the Kraft-AQ Yield-Kappa Number Relationship

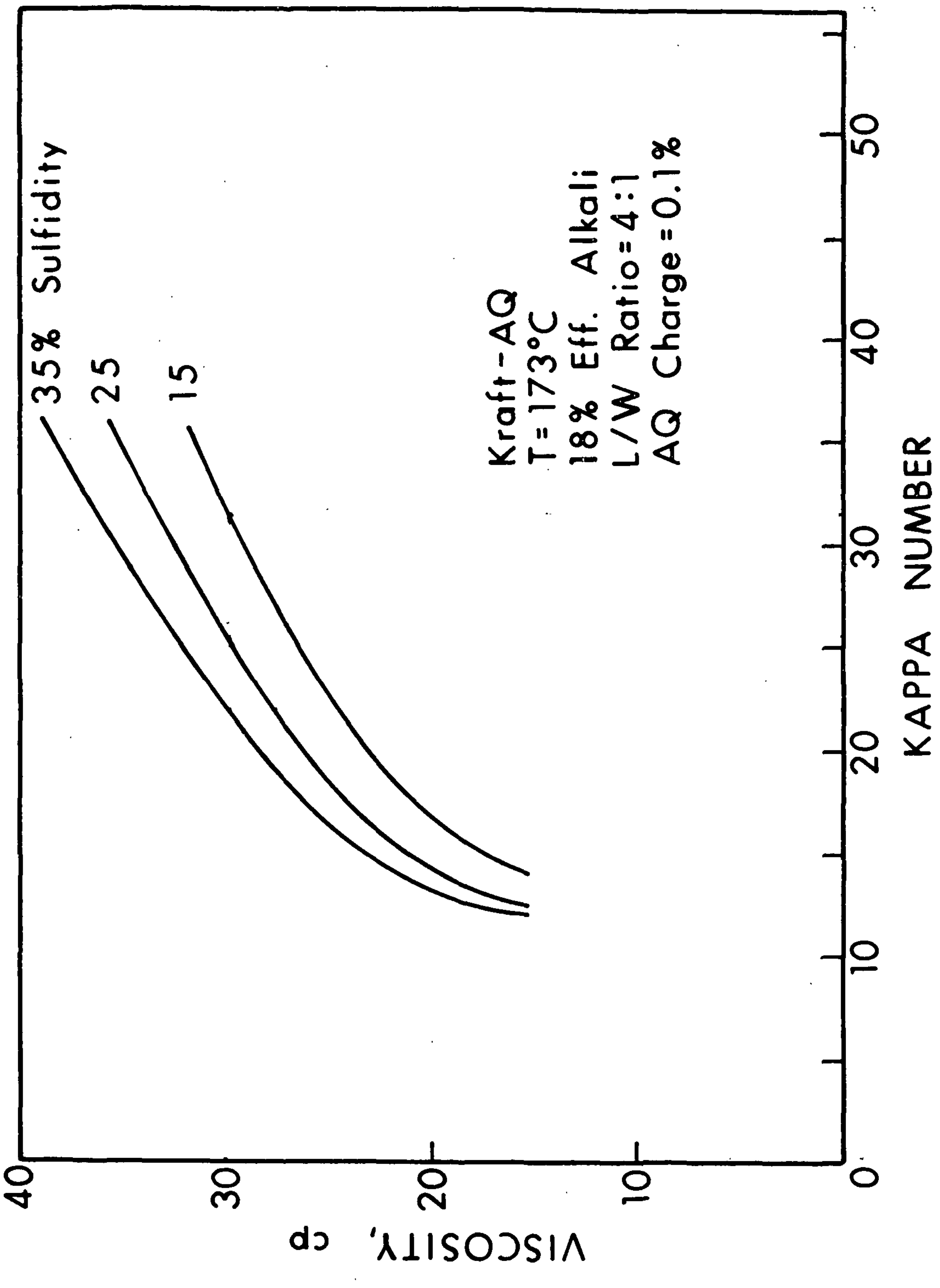

Figure 12. Effect of Sulfidity on the Kraft-AQ Viscosity-Kappa Number Relationship

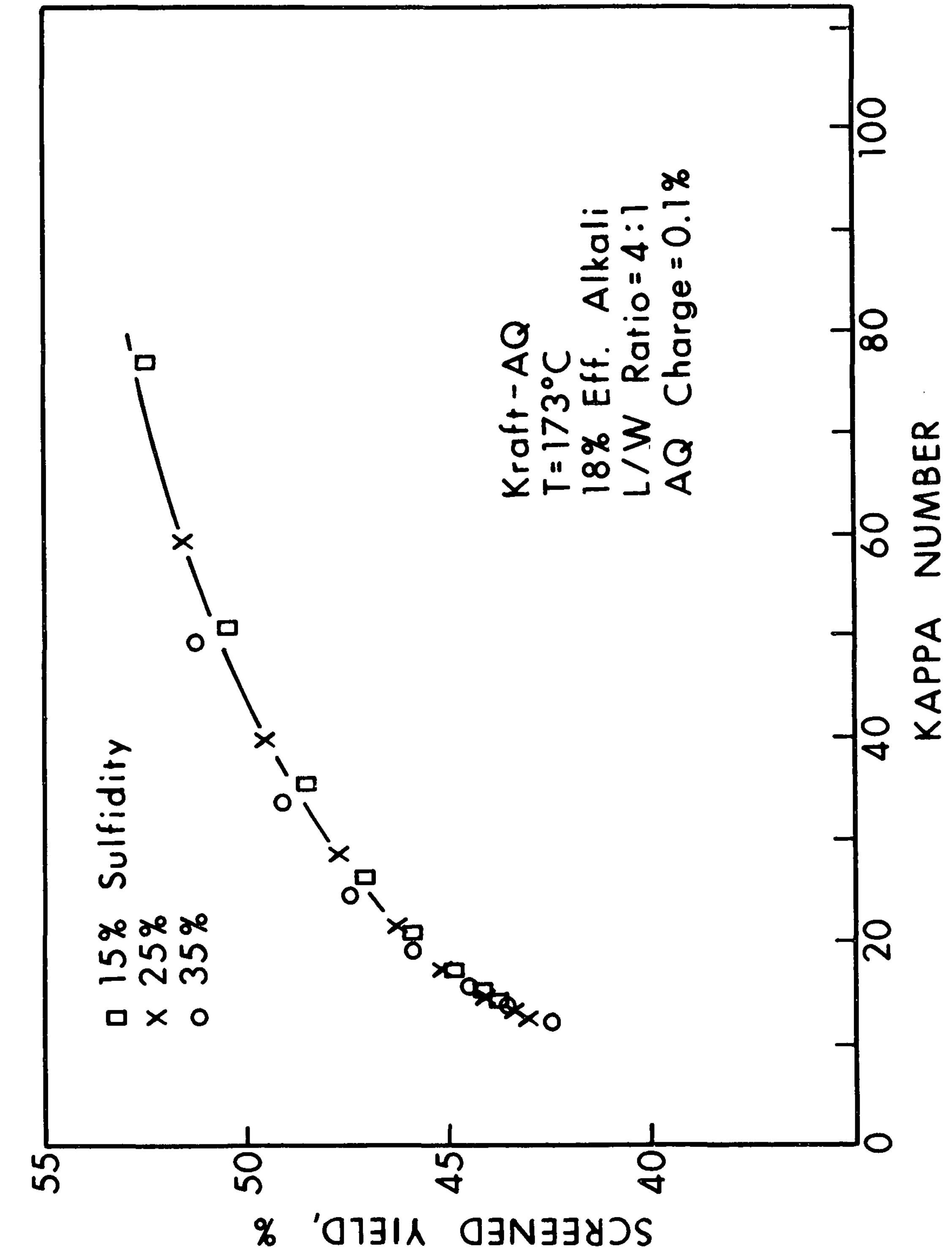

Figure 13. Effect of Sulfidity on the Kraft-AQ Yield-Kappa Number Relationship

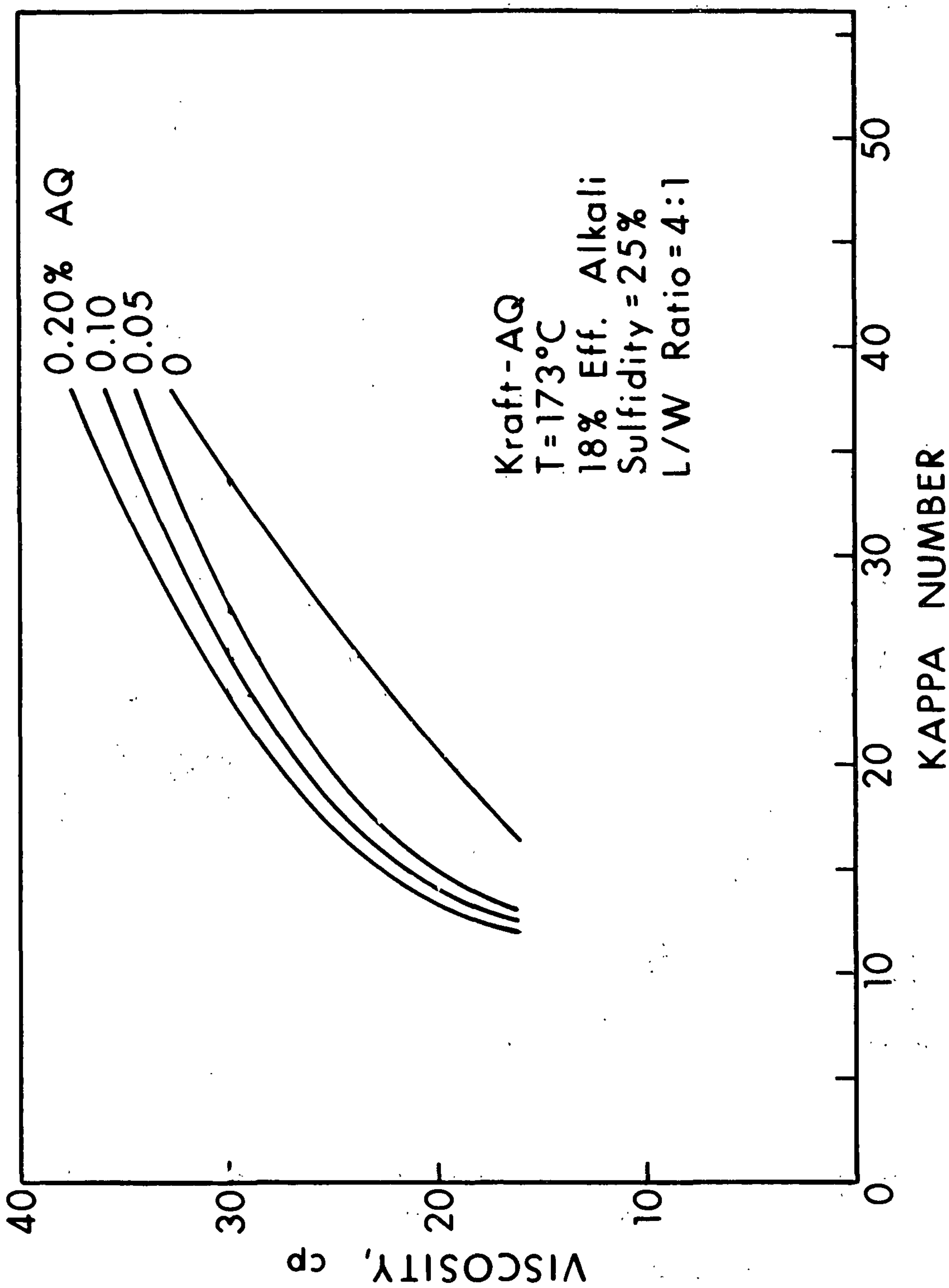

Figure 14. Effect of Anthraquinone Charge on the Viscosity-Kappa Number Relationship

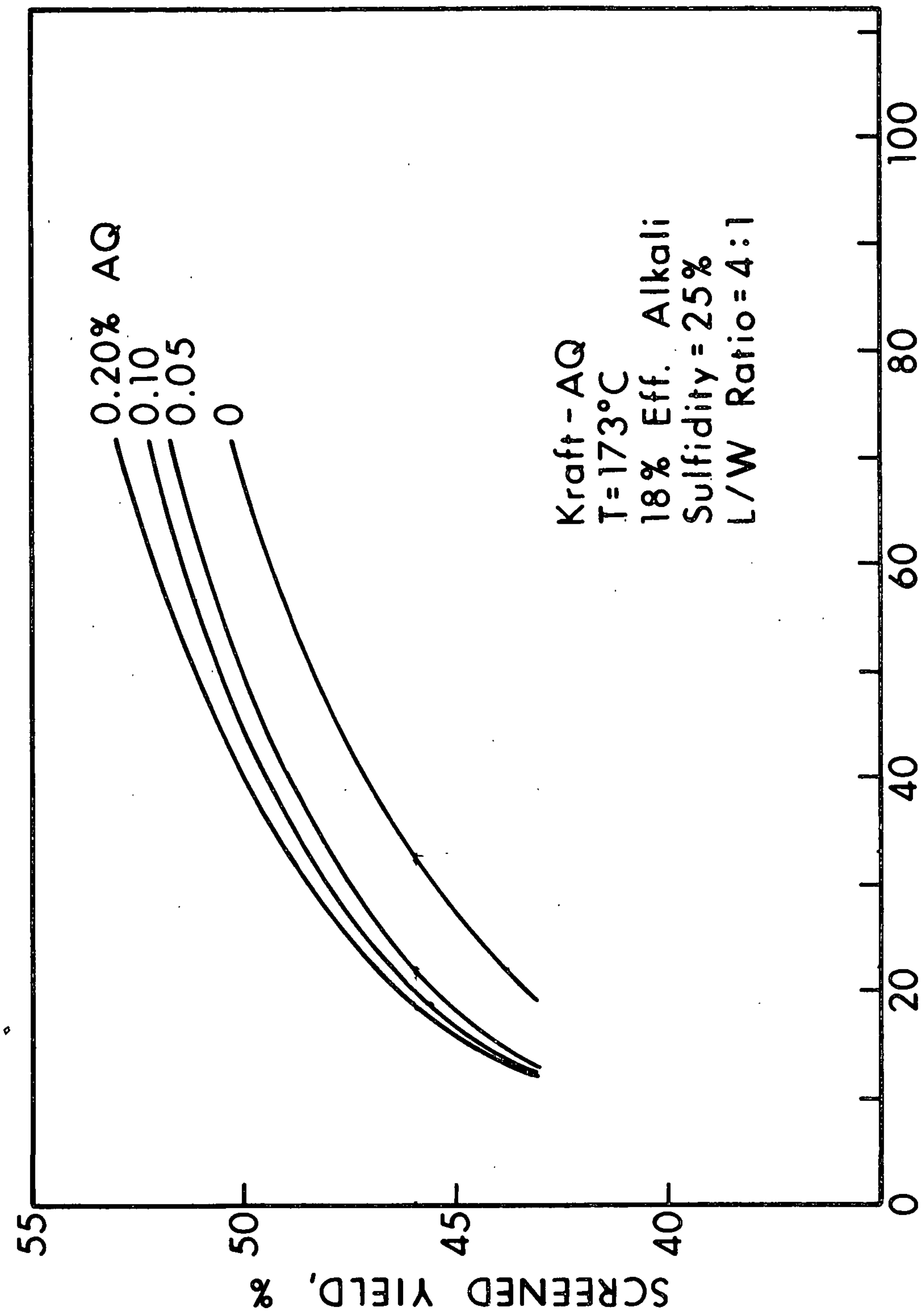

Figure 15. Effect of Anthraquinone Charge on the Yield-Kappa Number Relationship

Optimization

The results of optimization analysis of the kraft-anthraquinone polynomial model are shown in Table X, along with the same conventional kraft data included in Table V. As in the kraft optimizations, the primary constraint was that on unbleached pulp viscosity; the effect of imposing additional constraints, in the form of upper limits on H-factor and sulfidity, was also investigated. When no secondary constraints were imposed, the conditions for minimizing unbleached kappa number at a viscosity of 30 involved long cooking time, low effective alkali, and high values of both anthraquinone charge and sulfidity. These conditions are predicted to produce a pulp with a lignin content less than half that of a conventional kraft pulp at the same viscosity and with practically no loss in carbohydrate yield. Relaxing the viscosity constraint allows progressively lower values of kappa number to be achieved by using higher effective alkali charges and slightly changed values of the other variables. Constraining the H factor to more or less conventional values causes a substantial increase in the minimum kappa number at any viscosity level but still yields large kappa number reductions relative to conventional kraft pulping. Simultaneous constraints on both sulfidity and H-factor further increased the minimum achievable kappa number.

Figures 16 and 17 contain the optimized viscosity number and yield kappa number curves corresponding to the data in Table X. It is apparent that large reductions in kappa number are possible without detrimental effects on either viscosity or yield.

PULPING UNDER OPTIMUM CONDITIONS

Cooks were carried out under certain of the conditions predicted to be optimum to verify the predictions and to provide samples of pulp for bleachability

TABLE X

KRAFT-ANTHRAQUINONE OPTIMIZATION RESULTS

Process Conditions[a] for Minimizing Kappa Number at Various Viscosity Levels Compared to Conventional Conditions

Secondary Constraint	Viscosity Constraint, cp (Lower Limit)	Predictions: Kappa Number	Predictions: Yield, %	Predictions: Carbohydrate Yield, %	Process Conditions: Time at 173°C, min	Process Conditions: Effective Alkali, %	Process Conditions: Anthraquinone, %	Process Conditions: Sulfidity, %
None	15	11.1	42.4	41.7	179	18.9	0.25	35.2
	20	12.0	43.2	42.4	168	17.7	0.29	35.0
	25	13.1	44.0	43.1	160	16.8	0.27	35.5
	30	14.6	44.7	43.7	151	16.1	0.24	36.1
	35	16.9	45.6	44.4	142	15.4	0.19	36.4
H ≤ 3000	15	11.7	42.9	42.1	140	19.9	0.21	38.3
	20	12.4	43.7	42.9	140	18.4	0.29	36.8
	25	13.3	44.3	43.4	140	17.3	0.30	35.9
	30	14.7	44.9	43.9	140	16.3	0.26	36.4
	35	16.8	45.6	44.4	150	15.5	0.20	36.3
H ≤ 2000	15	15.0	43.8	42.8	89	21.2	0.09	35.9
	20	15.4	44.8	43.7	90	20.0	0.20	38.0
	25	16.2	45.5	44.4	90	18.7	0.26	37.9
	30	17.3	46.1	44.9	90	17.5	0.30	36.1
	35	19.1	46.7	45.4	90	16.5	0.25	37.0
S ≤ 25 and H ≤ 2000	15	16.5	43.8	42.7	89	21.8	0.08	25.0
	20	16.9	43.8	42.7	89	21.3	0.05	25.0
	25	17.9	45.9	44.7	89	19.0	0.36	25.0
	30	19.4	46.7	45.3	89	17.3	0.37	25.0
	35	22.8	47.6	46.0	89	15.8	0.30	25.0
Conventional kraft	20	17.6	42.2	41.1	210	16.0	0.00	25.0
	25	25.3	44.4	42.7	135	16.0	0.00	25.0
	30	32.2	46.2	44.0	99	16.0	0.00	25.0
	35	41.1	47.6	44.7	74	16.0	0.00	25.0

[a]Constant conditions: Maximum temperature 173°C.
Time to maximum temperature 90 minutes.
Liquor-to-wood ratio 4 cc/g.

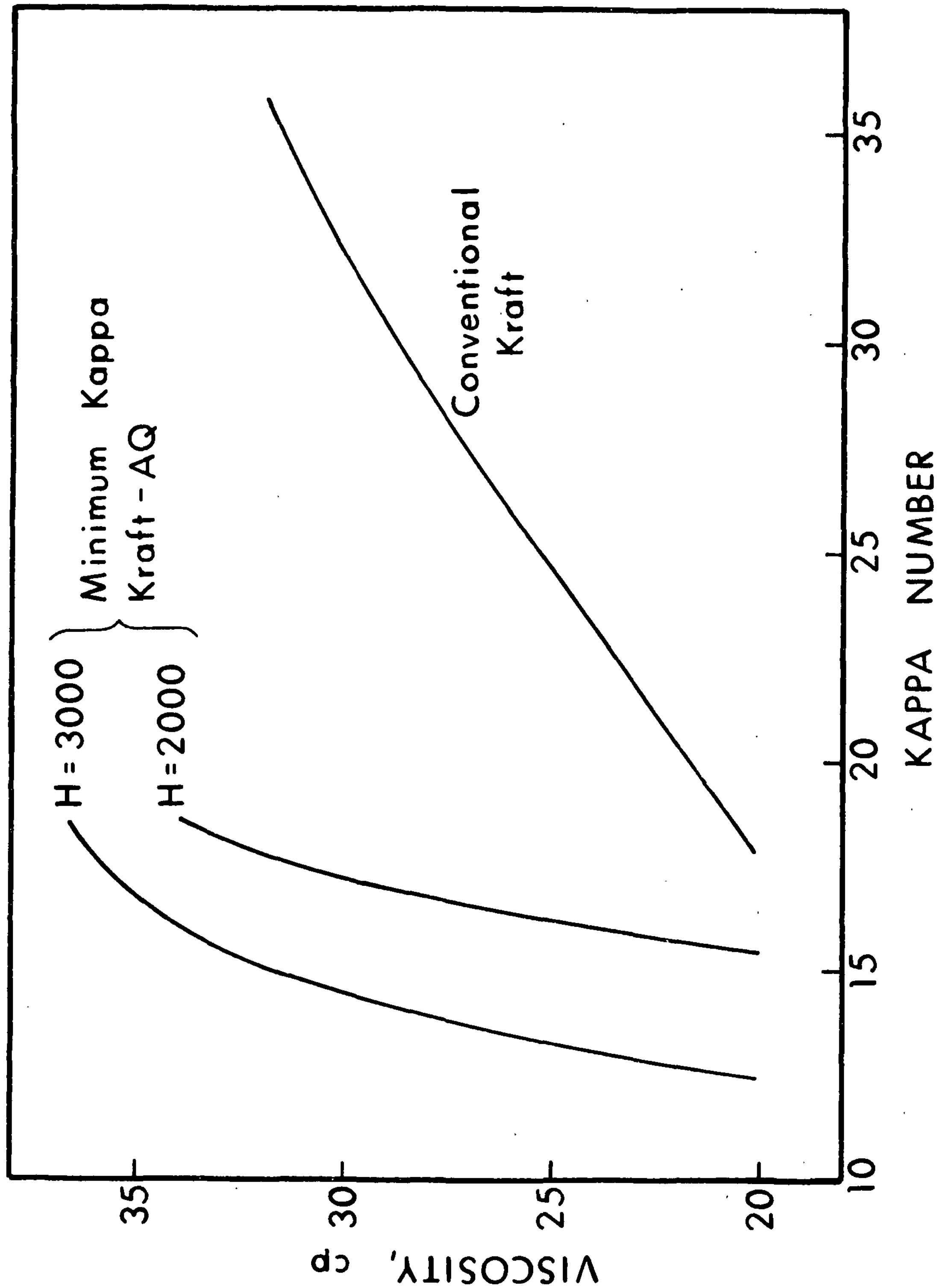

Figure 16. Optimized and Conventional Kraft-AQ Viscosity-Kappa Number Relationships. In the Conventional Case, Kappa Number was Varied by Varying Cooking Time. The Optimized Pulping Procedure Involves Holding the Cooking Time Constant at Values Corresponding to the H-Factor Values Shown and Varying the Liquor-to-Wood Ratio and Liquor Composition

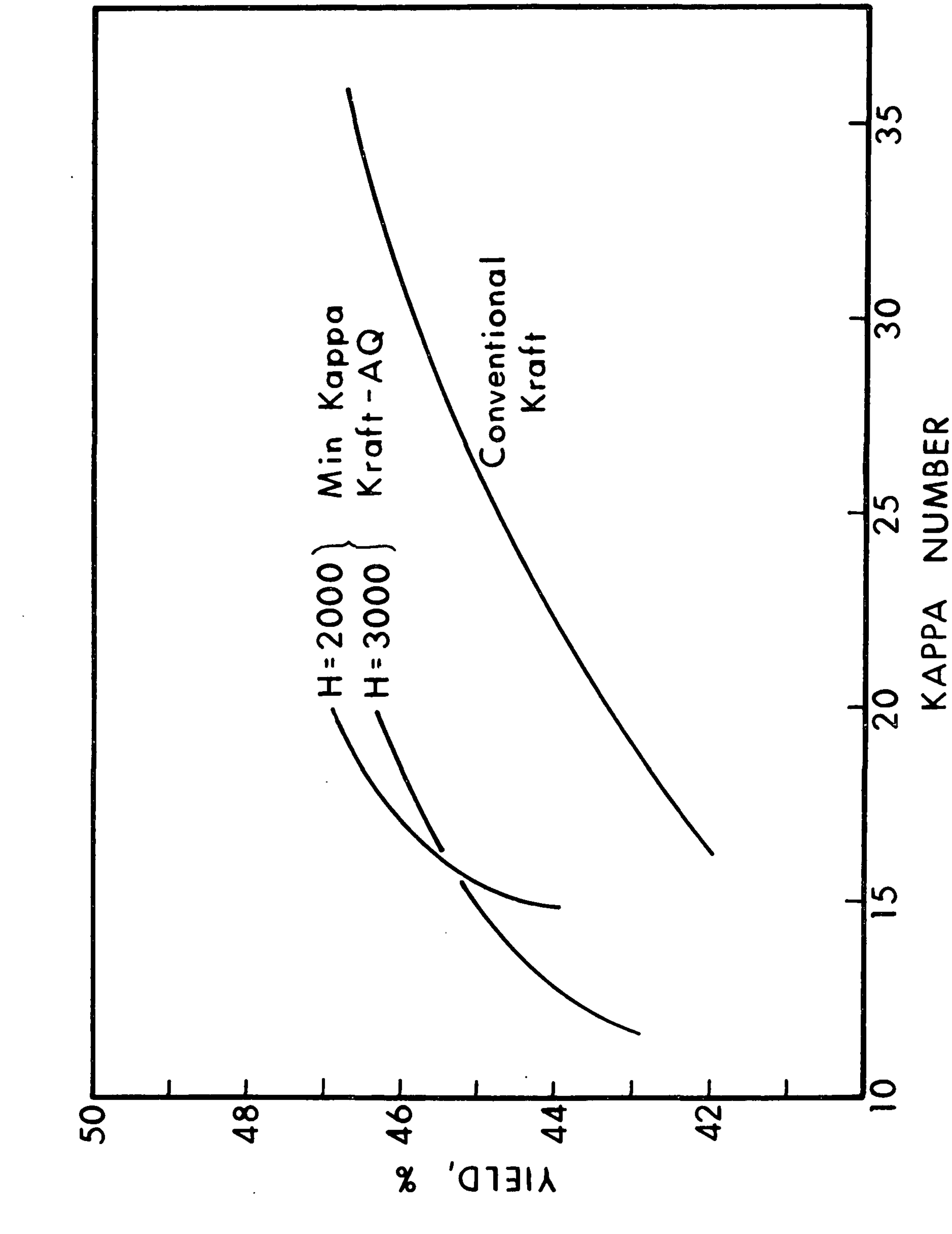

Figure 17. Optimized and Conventional Kraft-AQ Yield-Kappa Number Relationships. In the Conventional Case, Kappa Number was Varied by Varying Cooking Time. The Optimized Pulping Procedure Involves Holding the Cooking Time Constant at Values Corresponding to the H-Factor Values Shown and Varying the Liquor-to-Wood Ratio and Liquor Composition

and strength studies. Unbleached target viscosity values of 30 and 20 were chosen. The former is typical of the viscosities of unbleached softwood kraft pulps. The latter was chosen to test the acceptability of lower than normal viscosity levels in a pulp of low unbleached lignin content that may be expected to undergo less degradation in subsequent bleaching because of the smaller amount of lignin to be removed. H-factor constrained optima were chosen for verification in view of the probability that mills adopting low-lignin pulping technology would have limited digester capacity available. The H-factor levels chosen were 2000 (about 90 minutes at 173°C), which corresponds roughly to commercial practice for the preparation of bleachable grade softwood pulps, and 3000 (about 140 minutes at 173°C), which represents an extended cook. Cooks were done using a different sample of southern pine from that used for the cooks which gave the data upon which the models were based.

The results are shown in Table XI. The short minimum kappa (MK) kraft AQ cook with a target viscosity of 30 gave a pulp with kappa number and viscosity close to the predicted values and yield somewhat higher than predicted. The same was true of the corresponding cook at the lower viscosity level. At the longer cooking time kappa numbers were as expected, but viscosities were lower by 5 to 7 cp and yields were somewhat higher. For the conventional kraft cooks the yields and viscosities were both slightly higher than predicted on the basis of the model. The short MK kraft cook with a target viscosity of 30 gave the expected yield and viscosity levels but a kappa number somewhat more than predicted. The corresponding cook at the lower viscosity level gave a higher yield than expected but approximately the expected values of kappa number and viscosity. The long MK kraft cooks gave pulps with about the expected properties except that the yield was slightly higher than predicted.

TABLE XI

"MINIMUM KAPPA" (MK) KRAFT AND KRAFT-AQ COOKS

Cook Type	Viscosity Target, cp	Cook No.	Time at 173°C, min	Effective Alkali, %	AQ, %	Sulfidity, %	Liquor/ Wood, cc/g	Screened Yield, %	Rejects, %	Kappa No.	Viscosity, cp	Carbohydrate Yield, %
Short MK kraft-AQ	30	34	90	17.5	0.30	36.1	4.0	47.4	0.03	16.7	26	46.2
		44						47.2	0.02	16.9	27	46.0
		44A						48.4	0.10	19.0	28	47.0
		73						47.2	0.07	15.2	22	46.1
	20	35	90	20.0	0.20	38.0	4.0	45.9	0.00	13.1	19	45.0
		45						45.0	0.06	14.1	21	44.0
		45A						46.4	0.02	15.3	20	45.3
		74						44.9	0.02	13.0	15	44.0
Long MK kraft-AQ	30	36	140	16.3	0.26	36.4	4.0	46.9	0.01	15.7	23	45.8
	20	37	140	18.4	0.29	36.8	4.0	45.2	0.00	12.1	15	44.4
Conventional kraft	30	38	100	16.0	0.00	25.0	4.0	48.7	0.15	31.3	36	46.4
		46						48.6	0.06	33.1	37	46.2
		54						47.4	0.01	27.4	33	
	20	39	205	16.0	0.00	25.0	4.0	45.2	0.11	17.4	22	44.0
		47						45.5	0.03	17.8	26	44.3
		55						44.8	0.01	16.5	20	
Short MK kraft	30	40	90	19.2	0.00	39.9	5.0	46.5	0.10	22.4	32	44.9
		56						45.5	0.01	19.3	29	
	20	41	90	21.1	0.00	36.6	4.1	44.6	0.04	15.2	18	43.6
		57						44.0	0.00	16.4	17	
Long MK kraft	30	42	140	16.6	0.00	38.2	5.3	47.0	0.05	21.8	33	45.4
	20	43	140	19.5	0.00	39.2	5.1	45.2	0.01	15.2	23	44.2

In general, the agreement between actual and predicted pulping behavior was good except that the yields obtained were high. This can be attributed to a difference between the two wood samples used. Also, there was a tendency for the second wood sample to pulp more easily in the kraft process than the first. Nevertheless, these results clearly demonstrate that large kappa number reductions are possible at acceptable viscosity levels.

BLEACHING OF MINIMUM KAPPA PULPS

To verify that low-lignin pulping would result in the anticipated bleaching chemical cost saving in the first stages of the bleaching sequence and that it would not impair bleachability in subsequent stages, the bleachability of some of the pulps of Table XI was studied. Initially, only the first two stages of the sequence, the chlorine and caustic extraction stages, were investigated. A series of experiments was performed in which both the charge of chlorine in the chlorination stage and the charge of caustic in the caustic extraction stage were varied. The ratio of chlorine to kappa number was set at either 0.2 or 0.25, and the ratio of caustic in the extraction stage to chlorine charge in the chlorination stage was set at either 0.5 or 0.6. The permanganate numbers and viscosities of the resulting caustic extracted pulps were then measured. Results are contained in Tables XII through XIV.

A few general observations may be made with reference to these data. Increasing the chlorine charge from the low level to the high level decreased the extracted $KMnO_4$ (K) number by 10 to 25%. Increasing the caustic charge from the low level to the high level had little or no effect. Comparisons of the bleachability of the various pulps can thus be made with reference only to the data at the low levels of chlorine and caustic. An additional general observation is that for all pulps the drop in viscosity across the CE partial sequence was small.

TABLE XII

PREBLEACHING OF CONVENTIONAL KRAFT PULPS

	Unbleached Pulp Data			Chlorination[a]		Caustic Extraction[b]			
Type	From Cook	Kappa No.	Viscosity, cp	Cl_2 Applied, % on o.d. pulp	Residual Cl_2, % on o.d. pulp	NaOH Applied, % on o.d. pulp	End pH	$KMnO_4$ No.	Viscosity, cp
Short CK	38	31.3	36	6.26	0.06	3.13	11.9	6.0	34
						3.76	12.1	5.8	31
				7.82	0.34	3.91	12.0	4.3	31
						4.69	12.2	4.4	27
Long CK	39	17.4	22	3.48	0.07	1.74	11.7	5.6	22
						2.09	11.8	5.0	23
				4.35	0.23	2.18	11.8	3.9	19
						2.61	12.0	3.7	19

[a]45 Minutes, 25°C, 3% consistency.
[b]60 Minutes, 60°C, 10% consistency.

TABLE XIII

PREBLEACHING OF "MINIMUM KAPPA" (MK) KRAFT PULPS

	Unbleached Pulp Data			Chlorination[a]		Caustic Extraction[b]			
Type	From Cook	Kappa No.	Viscosity, cp	Cl_2 Applied, % on o.d. pulp	Residual Cl_2, % on o.d. pulp	NaOH Applied, % on o.d. pulp	End pH	$KMnO_4$ No.	Viscosity, cp
Short MK kraft cook	40	22.4	32	4.48	0.06	2.24	11.3	4.0	29
						2.69	11.7	4.2	30
				5.60	0.38	2.80	11.6	3.4	28
						3.36	11.8	3.3	27
	41	15.2	18	3.04	0.06	1.52	11.2	4.2	18
						1.82	11.6	3.8	19
				3.80	0.22	1.90	11.4	2.9	16
						2.28	11.6	3.1	16
Long MK kraft cook	42	21.8	33	4.36	0.06	2.18	11.2	4.5	30
						2.62	11.5	4.4	33
				5.45	0.27	2.72	11.5	3.6	27
						3.27	11.7	3.5	29
	43	15.2	23	3.04	0.06	1.52	11.2	4.1	21
						1.82	11.4	3.9	22
				3.80	0.33	1.90	11.4	3.3	20
						2.28	11.6	2.9	20

[a]45 Minutes, 25°C, 3% consistency.
[b]60 Minutes, 60°C, 10% consistency.

TABLE XIV

PREBLEACHING OF "MINIMUM KAPPA" (MK) KRAFT-AQ PULPS

	Unbleached Pulp Data			Chlorination[a]		Caustic Extraction[b]			
Type	From Cook	Kappa No.	Viscosity, cp	Cl_2 Applied, % on o.d. pulp	Residual Cl_2, % on o.d. pulp	NaOH Applied, % on o.d. pulp	End pH	$KMnO_4$ No.	Viscosity, cp
Short MK kraft cook	34	16.7	26	3.34	0.06	1.67	11.5	3.6	27
						2.00	11.7	3.4	27
				4.18	0.34	2.09	11.7	3.2	25
						2.51	11.9	3.4	24
	35	13.1	19	2.62	0.06	1.31	11.4	3.6	18
						1.57	11.6	3.6	17
				3.28	0.23	1.64	11.7	3.0	17
						1.97	11.9	3.2	17
Long MK kraft AQ-cook	36	15.7	23	3.14	0.06	1.57	11.3	3.2	22
						1.88	11.4	3.5	22
				3.92	0.44	1.96	11.3	2.8	21
						2.35	11.6	3.0	21
	37	12.1	15	2.42	0.06	1.21	11.1	3.3	15
						1.45	11.4	3.2	15
				3.02	0.33	1.51	11.4	2.8	14
						1.81	11.6	2.6	14

[a]45 Minutes, 25°C, 3% consistency.
[b]60 Minutes, 60°C, 10% consistency.

Application of the low levels of chlorine and caustic to a conventional kraft pulp of kappa number 31 gave an extracted K number of 6.0. If the conventional kraft cook was extended to a kappa number of 17, the corresponding K number was 5.6, indicating that low-lignin pulping, when achieved by simply extending the cook, does not impair the ease of removal of the residual lignin in chlorination and caustic extraction stages. The corresponding extracted K numbers for pulps which had been produced at kappa number levels in the range of 15 to 22 using MK conditions were 4.0 to 4.5. When MK conditions were used in the kraft-anthraquinone system to produce pulp having kappa numbers ranging from 12 to 17, the corresponding extracted K numbers were in the range 3.2 to 3.6. These results show that the use of kappa-minimizing conditions in both the kraft and kraft-anthraquinone systems make the residual lignin easier to remove with chlorine and caustic. The kraft-anthraquinone pulps are delignified more readily than the kraft pulps. In summary, there appears to be a positive correlation between the unbleached kappa number and the permanganate number after caustic extraction.

Bleachability in the latter stages of the CEDED sequence was studied in experiments in which the amounts of chlorine dioxide in both the third and fifth stages were varied. In preparing the chlorinated and caustic extracted pulps, which were the raw materials for these studies, the amounts of chlorine and caustic applied were the minimum amounts that would give an extracted K number of 4.5 or lower.

The results, which are collected in Tables XV through XVII, showed that there were significant differences between the pulps in their response to brightening in the final stages of the bleach sequence. The differences at low chlorine dioxide charges were most pronounced, but they did not always correlate with the differences

TABLE XV

CEDED BLEACHING OF CONVENTIONAL KRAFT PULPS

	Unbleached Pulp		Chlorination[a]		Extraction[b]		Chlorine Dioxide		Extraction[b]		Chlorine Dioxide				
No.	Kappa No.	Viscosity, cp	Cl_2, %	Residual, % on pulp	NaOH, %	End pH	ClO_2, %	Residual, % on pulp	NaOH, %	End pH	ClO_2, %	Residual, % on pulp	Brightness	Aged Brightness	Viscosity, cp
38	31.3	36	7.82	0.46	3.91	11.9	0.8	0.00	0.4	10.8	0.2	0.00	85.6	80.6	
											0.4	0.03	86.6	82.1	28
											0.8	0.38	87.4	82.8	
							1.2	0.02	0.6	11.2	0.2	0.00	89.6	85.6	
											0.4	0.04	88.8	84.9	24
											0.8	0.43	89.7	84.9	
39	17.4	22	4.35	0.34	2.18	11.8	0.8	0.00	0.4	10.9	0.2	0.03	86.2	81.6	
											0.4	0.14	87.2	82.8	16
											0.8	0.40	87.2	82.8	
							1.2	0.09	0.6	11.3	0.2	0.06	87.6	83.7	
											0.4	0.16	88.9	85.5	16
											0.8	0.46	88.2	84.0	

[a]45 Minutes, 25°C, 3% consistency.
[b]60 Minutes, 60°C, 10% consistency.
[c]180 Minutes, 70°C, 10% consistency.

TABLE XVI

CEDED BLEACHING OF "MINIMUM KAPPA" KRAFT PULPS

	Unbleached Pulp		Chlorination[a]		Extraction[b]		Chlorine Dioxide		Extraction[b]		Chlorine Dioxide			Aged	
No.	Kappa No.	Viscosity, cp	Cl_2, %	Residual, % on pulp	NaOH, %	End pH	ClO_2, %	Residual, % on pulp	NaOH, %	End pH	ClO_2, %	Residual, % on pulp	Brightness	Brightness	Viscosity, cp
40	22.4	32	4.48	0.04	2.24	11.2	0.8	0.00	0.4	10.6	0.2	0.00	81.8	79.3	
											0.4	0.04	84.8	81.9	25
											0.8	0.24	86.0	83.9	
							1.2	0.00	0.6	11.0	0.2	0.02	86.6	85.4	
											0.4	0.11	87.6	86.0	26
											0.8	0.35	88.6	85.8	
41	15.2	18	3.04	0.06	1.52	11.2	0.8	0.00	0.4	10.7	0.2	0.00	83.0	78.9	
											0.4	0.08	84.6	81.2	17
											0.8	0.34	85.8	82.1	
							1.2	0.00	0.6	10.9	0.2	0.02	87.2	84.6	
											0.4	0.13	87.9	84.0	16
											0.8	0.37	87.8	84.8	
42	21.8	33	4.36	0.11	2.18	11.2	0.8	0.00	0.4	10.6	0.2	0.00	83.4	79.2	
											0.4	0.07	85.3	81.0	28
											0.8	0.35	85.6	81.0	
							1.2	0.00	0.6	10.9	0.2	0.03	87.4	84.9	
											0.4	0.14	88.0	85.3	25
											0.8	0.43	88.6	85.7	
43	15.2	23	3.04	0.04	1.52	11.2	0.8	0.00	0.4	10.7	0.2	0.00	83.5	79.0	
											0.4	0.10	85.4	81.2	18
											0.8	0.25	85.9	81.5	
							1.2	0.01	0.6	11.0	0.2	0.04	87.5	84.2	
											0.4	0.13	88.0	84.5	18
											0.8	0.36	88.1	84.7	

[a]45 Minutes, 25°C, 3% consistency.
[b]60 Minutes, 60°C, 10% consistency.
[c]180 Minutes, 70°C, 10% consistency.

TABLE XVII

CEDED BLEACHING OF "MINIMUM KAPPA" KRAFT-AQ PULPS

	Unbleached Pulp		Chlorination[a]		Extraction[b]		Chlorine Dioxide		Extraction[b]		Chlorine Dioxide			Aged	
No.	Kappa No.	Viscosity, cp	Cl_2, %	Residual, % on pulp	NaOH, %	End pH	ClO_2, %	Residual, % on pulp	NaOH, %	End pH	ClO_2, %	Residual, % on pulp	Brightness	Aged Brightness	Viscosity, cp
34	16.7	26	3.34	0.06	1.67	11.4	0.8	0.00	0.4	10.9	0.2	0.03	84.2	81.8	
											0.4	0.14	86.0	82.7	24
											0.8	0.30	85.3	81.8	
							1.2	0.05	0.6	11.3	0.2	0.05	87.2	84.1	
											0.4	0.17	87.7	84.5	22
											0.8	0.44	87.7	83.4	
35	13.1	19	2.62	0.06	1.31	11.3	0.8	0.00	0.4	10.9	0.2	0.06	87.0	84.3	
											0.4	0.14	87.7	85.0	15
											0.8	0.41	87.3	84.3	
							1.2	0.18	0.6	11.2	0.2	0.06	88.3	85.1	
											0.4	0.20	88.0	84.9	15
											0.8	0.38	88.8	85.9	
36	15.7	23	3.14	0.06	1.57	11.2	0.8	0.00	0.4	10.8	0.2	0.04	85.6	83.1	
											0.4	0.18	85.0	82.3	19
											0.8	0.43	86.9	84.0	
							1.2	0.05	0.6	11.0	0.2	0.06	86.5	83.4	
											0.4	0.17	87.9	85.5	19
											0.8	0.46	86.8	84.2	
37	12.1	15	2.42	0.06	1.21	11.1	0.8	0.00	0.4	10.6	0.2	0.04	86.3	83.8	
											0.4	0.15	86.0	84.1	15
											0.8	0.47	85.6	81.5	
							1.2	0.12	0.6	10.9	0.2	0.04	87.3	84.9	
											0.4	0.14	87.0	85.9	14
											0.8	0.37	88.6	86.4	

[a]45 Minutes, 25°C, 3% consistency.
[b]60 Minutes, 60°C, 10% consistency.
[c]180 Minutes, 70°C, 10% consistency.

at high chlorine dioxide charges. For example, application of 1% chlorine dioxide to the pulp from Cook 40, which was a short MK kraft cook, gave a brightness of 81.8, whereas application of the same amount to the pulp from Cook 35, which was a low viscosity MK kraft-anthraquinone cook, gave a brightness of 87.0. When large amounts of chlorine dioxide were used, these two pulps gave virtually the same brightness. On the other hand, pulp from Cook No. 34, a high viscosity MK kraft-anthraquinone cook, when compared to that from Cook No. 40, gave a higher brightness at low chlorine dioxide charges but lower brightness at high charges.

To facilitate a comparison of the pulps, the data of Tables XV through XVII were used to estimate for each pulp the maximum final brightness practically attainable and the total amount of chlorine dioxide required to reach a final brightness of 87.5. This was done graphically, by using plots of the type shown in Fig. 18 and 19, which also serve to further illustrate how the effects of varying chlorine dioxide charge vary from pulp to pulp.

Table XVIII makes the desired comparison. It is apparent that reduction of the unbleached kappa number from 31 to 17 by simply extending a conventional kraft cook results in a reduction in brightness ceiling and an increase in the chlorine dioxide requirement. If, instead, the unbleached kappa number reduction was achieved using kappa number minimizing conditions in either the kraft or the kraft-anthraquinone systems, similar reductions in brightness ceiling and increases in chlorine dioxide consumption were observed, with one exception. The exception was the kraft-anthraquinone pulp produced at the lower of the two kappa numbers in a short cook. This pulp exhibited no increase in chlorine consumption and only a slightly reduced brightness ceiling. It may be significant that it was the only one produced using both the high effective alkali level and addition of anthraquinone.

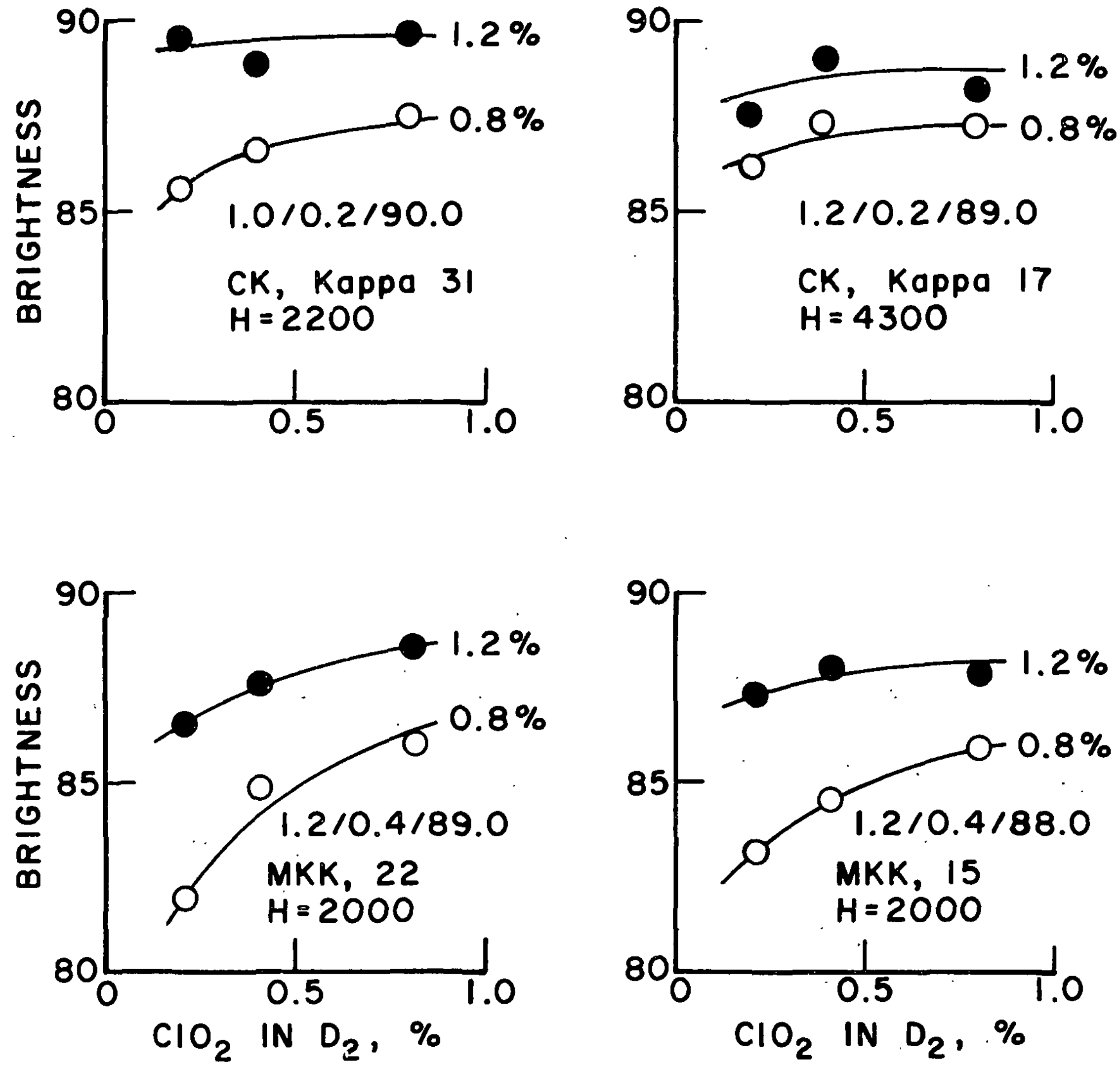

Figure 18. Chlorine Dioxide Response Curves for Conventional Kraft (CK) and Low-Lignin Kraft (MKK) Pulps. Figures Adjacent to the Curves Represent the ClO_2 Charge in the Third Stage. Figures Shown Below the Curves are Respectively, the ClO_2 Requirements to Reach 87.5 Brightness and the Estimated Brightness Ceiling.

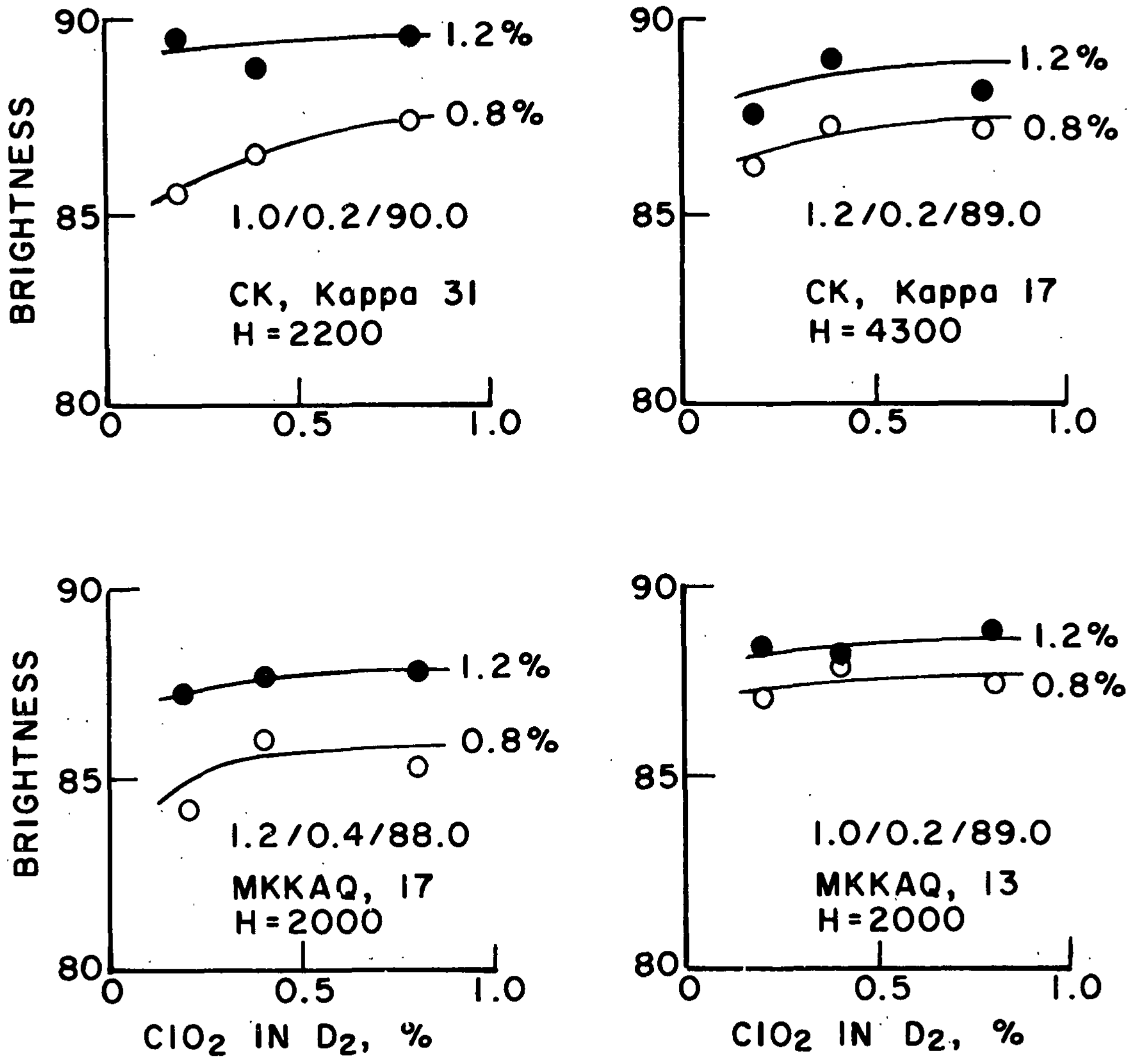

Figure 19. Chlorine Dioxide Response Curves for Conventional Kraft (CK) and Low-Lignin Kraft-AQ (MKKAQ) Pulps. Figures Adjacent to the Curves Represent the ClO_2 Charge in the Third Stage. Figures Shown Below the Curves are Respectively, the ClO_2 Requirements to Reach 87.5 Brightness and the Estimated Brightness Ceiling.

TABLE XVIII

BLEACHABILITY OF CONVENTIONAL AND "MINIMUM KAPPA" PULPS

Cook Type	H-Factor	Unbleached Kappa No.	Estimated Brightness Ceiling	Estimated ClO_2 Required for 87.5 Brightness, %
CK	2200	31	90.0	1.2
	4200	17	89.0	1.4
MKK[a]	2000	22	89.0	1.6
		15	88.0	1.6
MKK	3000	22	89.0	1.4
		15	88.5	1.4
MKKAQ[b]	2000	17	88.0	1.6
		13	89.0	1.2
MKKAQ	3000	16	88.0	1.6
		12	88.5	1.6

[a]Minimum kappa kraft.
[b]Minimum kappa kraft-anthraquinone.

As noted above, these chlorine dioxide response studies were done using chlorine charges chosen to give an approximately constant caustic extracted K number. It was subsequently pointed out to us, however, that the comparison might be better made at a constant ratio of chlorine to kappa number or constant chlorine residual to take advantage of the greater ease of first stage delignification, which some of the pulps exhibited. This possibility was tested in a new series of experiments on MK kraft-anthraquinone pulps prepared at both the normal and low viscosity levels. Ratios of chlorine charge to kappa number of 0.22 and 0.25 were used and the results compared to those obtained earlier when a ratio of 0.20 was used. The results of the new set of experiments are contained in Tables XIX and XX, and the comparisons with earlier data are made graphically in Fig. 20 and 21.

TABLE XIX

CEDED BLEACHING OF MKKAQ-30 PULP WITH INCREASED CHLORINE CHARGE

	Unbleached Pulp		Chlorination[a]		Extraction[b]			Chlorine Dioxide[c]		Extraction[b]		Chlorine Dioxide[c]			Aged	
No.	Kappa No.	Viscosity, cp	Cl_2, %	Residual, % on pulp	NaOH, %	End pH	$KMnO_4$ No.	ClO_2, %	Residual, % on pulp	NaOH, %	End pH	ClO_2, %	Residual, % on pulp	Brightness	Brightness	Viscosity, cp
73	15.2	22.0	3.34	0.23	1.67	11.5	3.3	0.8	0.00	0.4	11.5	0.2	0.02	84.1	81.9	
												0.4	0.12	85.5	82.7	17.4
												0.8	0.40	86.1	82.3	
								1.2	0.02	0.6	11.9	0.2	0.04	86.5	83.5	
												0.4	0.15	87.2	85.7	16.2
												0.8	0.42	87.8	85.8	
			3.80	0.58	1.90	11.8	2.8	0.8	0.02	0.4	11.7	0.2	0.04	87.3	85.1	
												0.4	0.14	86.6	83.9	16.6
												0.8	0.36	87.0	84.8	
								1.2	0.20	0.6	11.8	0.2	0.06	88.8	86.6	
												0.4	0.20	87.2	86.2	15.1
												0.8	0.38	88.3	85.6	

[a]45 Minutes, 25°C, 3% consistency.
[b]60 Minutes, 60°C, 10% consistency.
[c]180 Minutes, 70°C, 10% consistency.

TABLE XX

CEDED BLEACHING OF MKKAQ-20 PULP WITH INCREASED CHLORINE CHARGE

	Unbleached Pulp		Chlorination[a]		Extraction[b]			Chlorine Dioxide		Extraction[b]		Chlorine Dioxide			Aged	
No.	Kappa No.	Viscosity, cp	Cl_2, %	Residual, % on pulp	NaOH, %	End pH	$KMnO_4$ No.	ClO_2, %	Residual, % on pulp	NaOH, %	End pH	ClO_2, %	Residual, % on pulp	Brightness	Brightness	Viscosity, cp
74	13.0	15.0	2.86	0.33	1.43	11.6	2.7	0.8	0.02	0.40	11.7	0.2	0.04	87.2	84.3	
												0.4	0.14	88.0	85.2	11.7
												0.8	0.36	88.3	85.8	
								1.2	0.20	0.60	11.9	0.2	0.04	88.5	85.5	
												0.4	0.10	88.5	86.0	11.4
												0.8	0.44	88.3	86.1	
			3.25	0.52	1.54	11.7	2.1	0.8	0.03	0.40	11.6	0.2	0.04	87.9	84.1	
												0.4	0.11	87.8	85.6	12.0
												0.8	0.40	88.4	85.1	
												0.2	0.04	87.9	84.5	
												0.4	0.11	88.0	84.4	11.1
												0.8	0.38	88.4	85.6	

[a]45 Minutes, 25°C, 3% consistency.
[b]60 Minutes, 60°C, 10% consistency.
[c]180 Minutes, 70°C, 10% consistency.

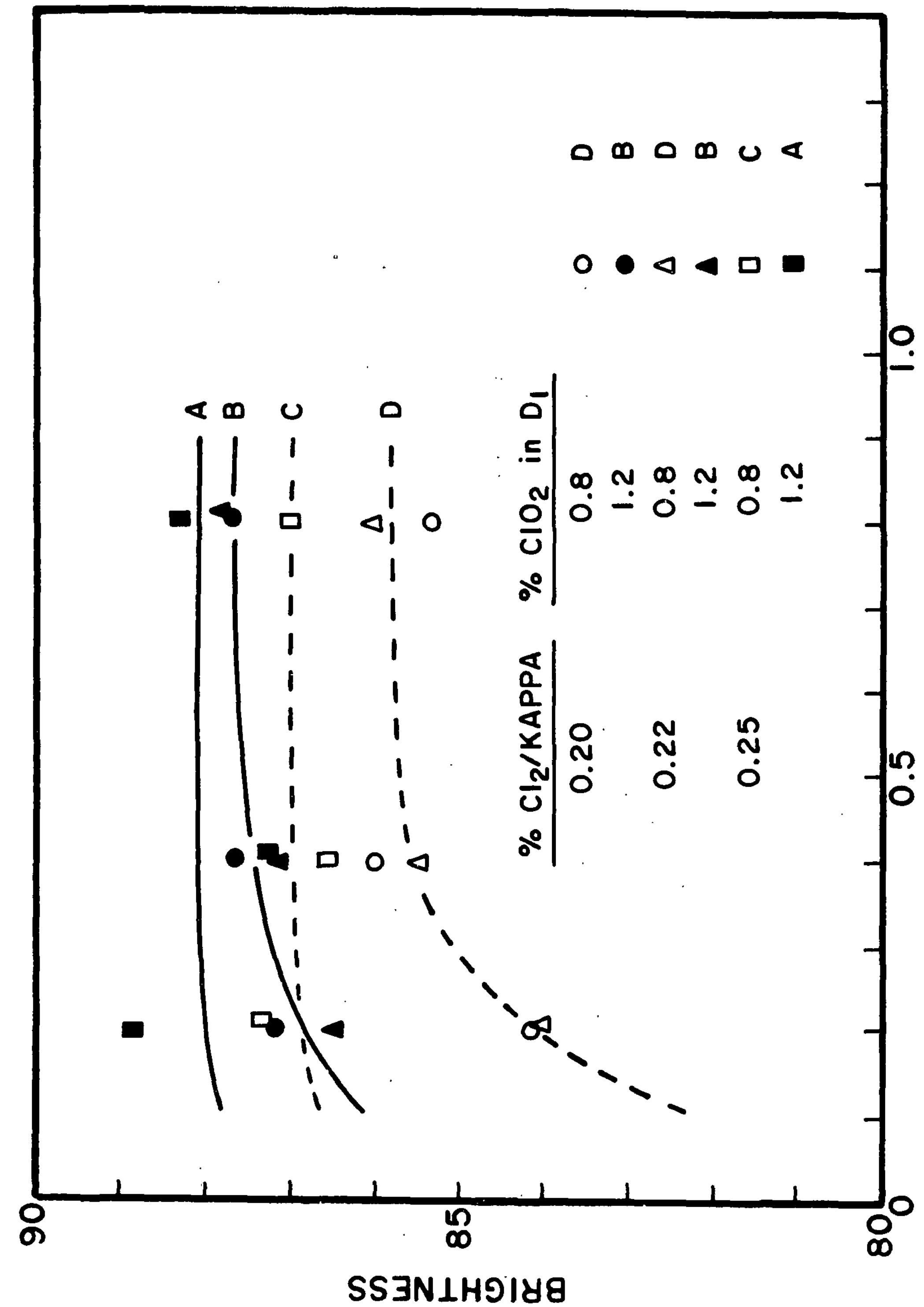

Figure 20. Effects of Cl_2 Charge and Charge of ClO_2 in the First ClO_2 Stage (D_1) on Brightness Response in the Second ClO_2 Stage (D_2) of MKKAQ-30 Pulp from a Short Cook. Sequence: CEDED

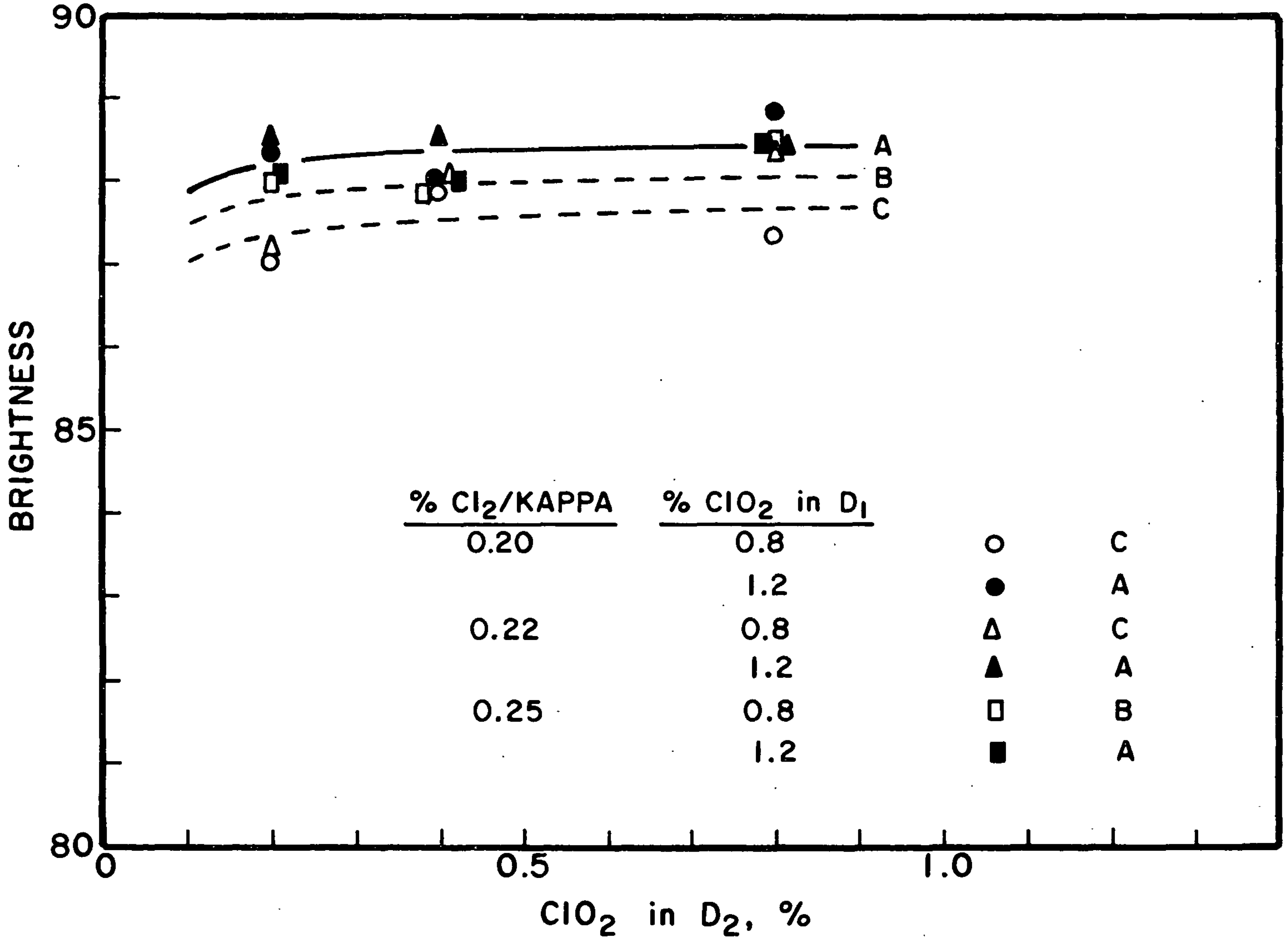

Figure 21. Effects of Cl_2 Charge and Charge of ClO_2 in the First ClO_2 Stage (D_1) on Brightness Response in the Second ClO_2 Stage (D_2) of MKKAQ-20 Pulp from a Short Cook. Sequence: CEDED

As shown in Fig. 20, application of the largest amount of chlorine to the MKKAQ-30 pulp significantly improved its response to chlorine dioxide at low chlorine dioxide charges, but the improvement was small at the highest chlorine dioxide charges. Thus, for this pulp, increasing the chlorine charge reduces the amount of chlorine dioxide necessary to achieve a brightness of 87.5 but has little effect on the brightness ceiling. For the more extensively delignified unbleached pulp, on the other hand, Fig. 21 shows that increasing the chlorine charge had little effect on either quantity.

It may be concluded from these results that, with a suitable adjustment of chlorination conditions, low-lignin kraft-anthraquinone pulps require no more chlorine dioxide to reach a moderately high brightness target (87.5) than do conventional kraft pulps. The highest practically attainable brightness, however, is slightly lower for the low-lignin kraft-anthraquinone pulps than for the conventional kraft pulps. It seems reasonable to expect that the same would also be true for low-lignin kraft pulps.

PHYSICAL PROPERTIES OF MINIMUM KAPPA PULPS

Samples of MK kraft and kraft-anthraquinone pulps having target viscosity levels of 30 and 20 were prepared for strength evaluation both before and after bleaching in a CEDED sequence. For comparison, two conventional kraft control pulps were also prepared and evaluated at the two target viscosity levels. The results are shown in Table XXI.

Of particular interest is the comparison of the tear factors of the various pulps. Tear factor is shown as a function of tensile strength (expressed as breaking length) for the unbleached pulps in Fig. 22 and for the bleached pulps in Fig. 23. It is immediately apparent that large differences do not exist between pulp types.

TABLE XXI

PHYSICAL PROPERTIES OF CONVENTIONAL AND MINIMUM KAPPA PULPS

		Unbleached								Bleached							
Cook Type	Cook No.	PFI Revs.	CSF, mL	Density, g/cc	Burst Factor	Tear Factor	Breaking Length, km	Stretch, %	Zero-Span B.L., km	PFI Revs.	CSF, mL	Density, g/cc	Burst Factor	Tear Factor	Breaking Length, km	Stretch, %	Zero-Span B.L., km
CK-30	46	2250	650	0.585	57.8	171	7.93	2.33	19.7	2250	660	0.623	61.9	164	8.48	2.70	19.5
		5000	555	0.644	69.4	145	9.21	2.85	19.9	3500	400	0.642	68.7	138	8.99	2.81	19.4
		6000	460	0.645	70.7	138	9.78	2.88	19.7	4750	250	0.652	77.5	138	8.91	2.72	19.4
		7000	335	0.661	70.8	138	9.75	2.91	19.7	6000	235	0.679	73.8	133	9.36	3.04	19.5
	54	2500	670	0.591	58.1	178	8.11	2.39	19.9	3000	610	0.644	68.3	158	8.82	2.65	19.6
		3500	545	0.629	66.8	149	8.84	2.72	18.9	3750	520	0.657	67.6	144	9.07	2.84	20.1
		4500	455	0.640	66.7	151	9.12	2.82	19.8	5000	435	0.678	70.5	139	9.48	2.92	19.6
		5000	380	0.641	66.1	146	9.57	2.87	19.8	5750	345	0.686	72.8	129	9.86	3.10	19.7
		6500	245	0.661	72.7	130	9.99	2.91	19.6	7000	285	0.698	76.9	124	9.86	3.17	20.3
CK-20	47	2250	640	0.618	59.6	152	8.29	2.48	19.6	2250	650	0.625	59.3	149	8.08	2.48	19.3
		5000	560	0.656	71.3	135	9.88	2.78	19.8	3500	340	0.639	63.6	146	8.57	2.62	20.1
		6000	420	0.671	72.4	130	9.82	2.79	19.7	4750	240	0.677	68.4	130	9.20	2.97	19.1
		7000	315	0.697	72.6	115	10.07	2.82	19.9	6000	195	0.684	70.9	128	9.64	2.93	19.6
	55	2250	655	0.617	56.9	155	8.10	2.40	20.0	3000	610	0.645	60.2	142	8.36	2.68	18.6
		3250	535	0.633	60.0	146	8.89	2.58	20.3	3500	550	0.662	62.4	137	8.82	2.73	19.3
		4000	465	0.653	67.3	137	9.22	2.67	18.9	4500	450	0.668	65.7	129	8.69	2.79	20.0
		5000	320	0.671	69.9	122	9.32	2.61	20.0	5000	390	0.679	67.2	124	8.97	2.90	19.3
		6000	265	0.689	67.8	120	9.75	2.78	20.2	7000	245	0.700	72.1	118	9.37	2.96	19.7
MKK-30	56	2500	665	0.608	56.9	162	8.35	2.58	18.4	3000	640	0.632	65.4	157	8.50	2.75	19.8
		3250	610	0.632	64.5	154	8.65	2.63	19.9	4000	530	0.655	70.6	154	9.21	2.94	20.8
		4000	540	0.650	65.9	149	8.81	2.86	19.0	5000	465	0.659	71.2	149	9.15	2.94	20.3
		5000	425	0.646	70.1	155	9.08	2.91	20.2	7000	305	0.685	72.3	148	9.25	3.04	19.5
		7000	265	0.556	71.2	144	9.56	3.00	19.8	7750	260	0.689	73.7	134	9.57	3.08	20.2
MKK-220	57	2500	695	0.586	55.5	182	7.64	2.44	19.3	3000	635	0.633	57.0	152	8.15	2.66	20.0
		3250	600	0.628	57.2	139	8.17	2.62	18.5	4000	530	0.644	57.9	146	8.46	2.76	18.3
		4000	535	0.629	59.7	146	8.45	2.58	19.5	5000	465	0.655	63.0	142	8.55	2.90	20.5
		5000	435	0.648	66.4	141	8.81	2.74	19.4	6250	340	0.665	62.9	127	8.62	2.78	19.2
		6000	330	0.647	64.4	138	8.61	2.78	19.2	7000	285	0.677	65.9	130	8.87	2.85	20.4
		6000	260	0.655	67.4	141	9.02	2.80	19.8								
MKKAQ-30	44	2250	660	0.617	66.5	148	8.72	2.63	19.6	2250	640	0.627	62.6	150	8.04	2.49	19.9
		5000	550	0.655	68.7	125	9.40	2.75	19.5	3500	350	0.649	65.9	140	8.71	2.72	19.8
		6000	455	0.673	69.0	125	9.77	2.77	19.2	4750	250	0.660	64.9	134	8.99	2.85	19.6
		7000	320	0.691	73.3	119	10.07	2.96	19.2	6000	190	0.694	72.9	123	9.35	2.87	18.5
MKKAQ-20	45	2250	670	0.615	56.1	155	8.07	2.29	19.4	2250	640	0.606	56.7	151	7.82	2.49	19.3
		5000	570	0.656	64.2	129	9.31	2.74	19.0	3500	360	0.638	60.4	147	8.42	2.77	19.3
		6000	460	0.668	70.4	123	9.72	2.84	20.0	4750	245	0.656	62.1	132	8.87	2.96	20.4
		7000	320	0.688	72.8	124	9.58	2.72	19.5	6000	175	0.671	66.9	131	9.15	2.96	19.0

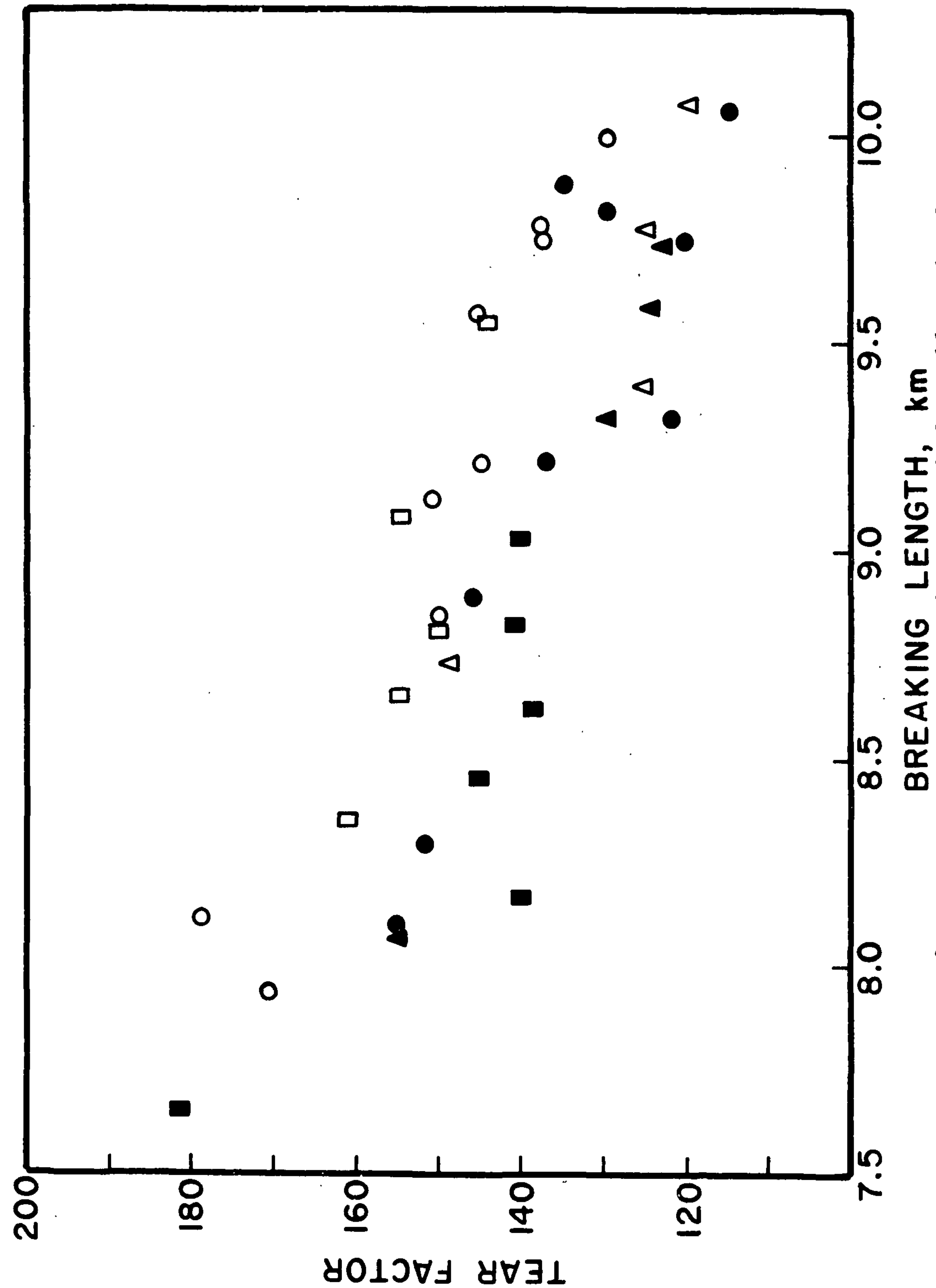

Figure 22. Tear Factor vs. Tensile Strength for Unbleaced Pulps
Key to Symbols: circles - conventional kraft pulps; squares - MKK pulps; triangles - MKKAQ pulps; open symbols - target viscosity 30; filled symbols - target viscosity 20

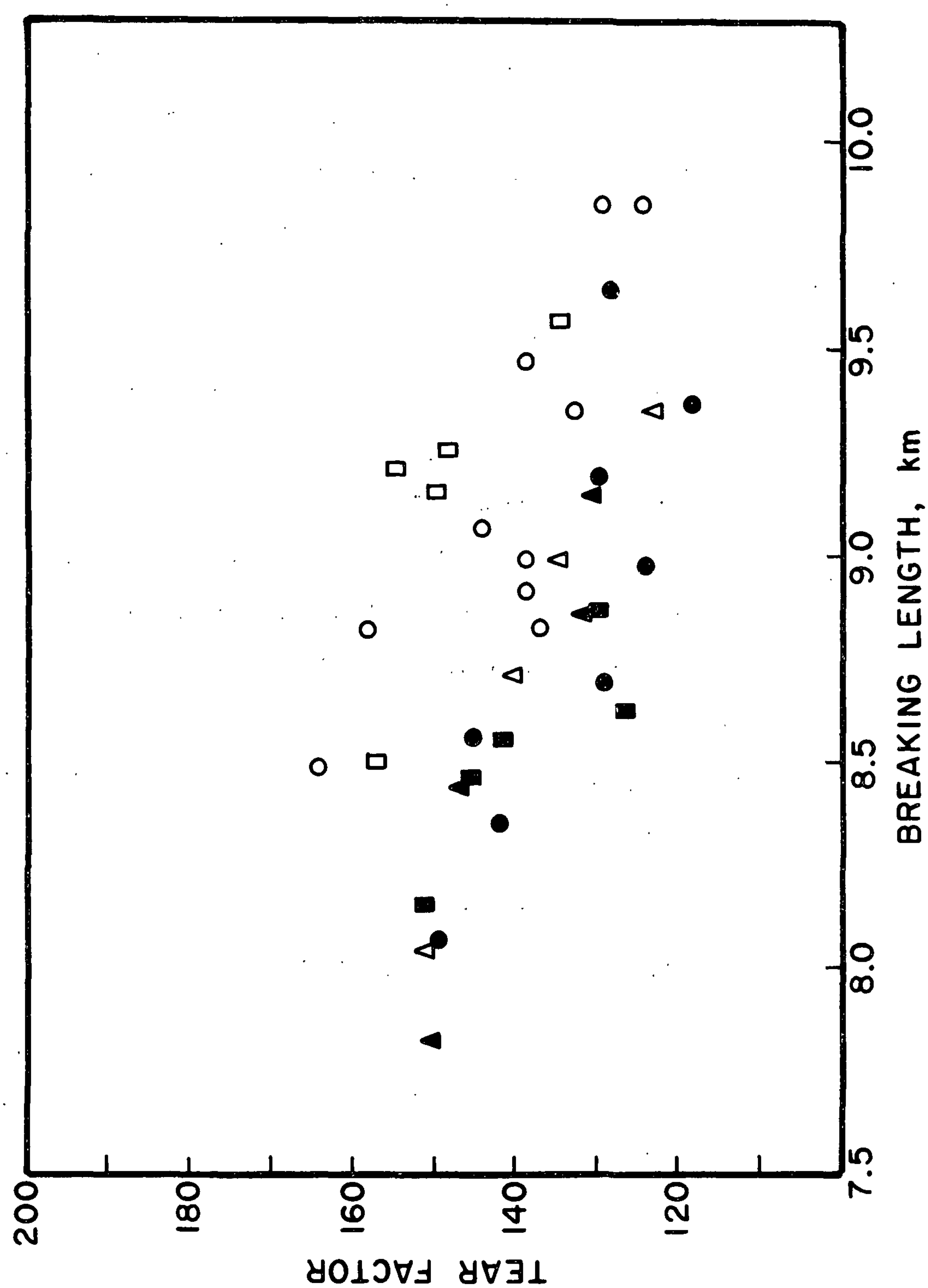

Figure 23. Tear Factor *vs.* Tensile Strength for Bleached Pulps
Key to Symbols: Same as Figure 22

A simplified comparison is presented in Table XXII. The tear factor values shown in this table were obtained by choosing a breaking length of 9 kilometers as a basis for comparison and using linear regression of the data for each pulp together with interpolation to arrive at the values shown. The data for the unbleached pulps can be broken down into two groups within which differences are probably not significant. The first of these includes the conventional and MK kraft pulps prepared at a target viscosity level of 30. These pulps had tear factors at 9 kilometers breaking length of approximately 150. The other group included the 30 target viscosity MK kraft-anthraquinone pulp and all pulps prepared at the target viscosity level of 20. These pulps had tear factors clustered around a value of 137. The bleached pulps could similarly be divided into two or possibly three groups. The first included the 30 viscosity conventional and MK kraft pulps at a value of 148 and the second, the kraft-anthraquinone pulps and the low viscosity conventional kraft pulps at a value of 132, and finally the low viscosity MK kraft pulp at a value of 123. The last two groups could probably be combined and considered to have a central value of about 130.

TABLE XXII

STRENGTHS OF MINIMUM KAPPA (MK) PULPS

Pulp Type	Kappa No.	Viscosity		Tear Factor at 9.0 km Breaking Length	
		Unbleached	Bleached	Unbleached	Bleached
Conventional kraft	30	35	24	152	146
	17	23	16	139	131
MK kraft-AQ	17	28	21	139	132
	14	21	17	136	133
MK kraft	19	29	21	151	151
	16	17	15	133	123

Figures 24 and 25 compare the tensile strengths of the various pulps as a function of sheet density. Again, the differences are not large. The low viscosity pulps tended to have slightly lower tensile strength at a given sheet density. This difference does not appear to be associated with individual fiber strength since the zero span strengths of all pulps were similar, as shown in Fig. 26 and 27.

In summary, the MK kraft pulp made under conditions corresponding to a target viscosity value of 30 was no weaker than the conventional kraft pulp. The other low-lignin pulps exhibited a loss in tearing resistance of approximately 10%.

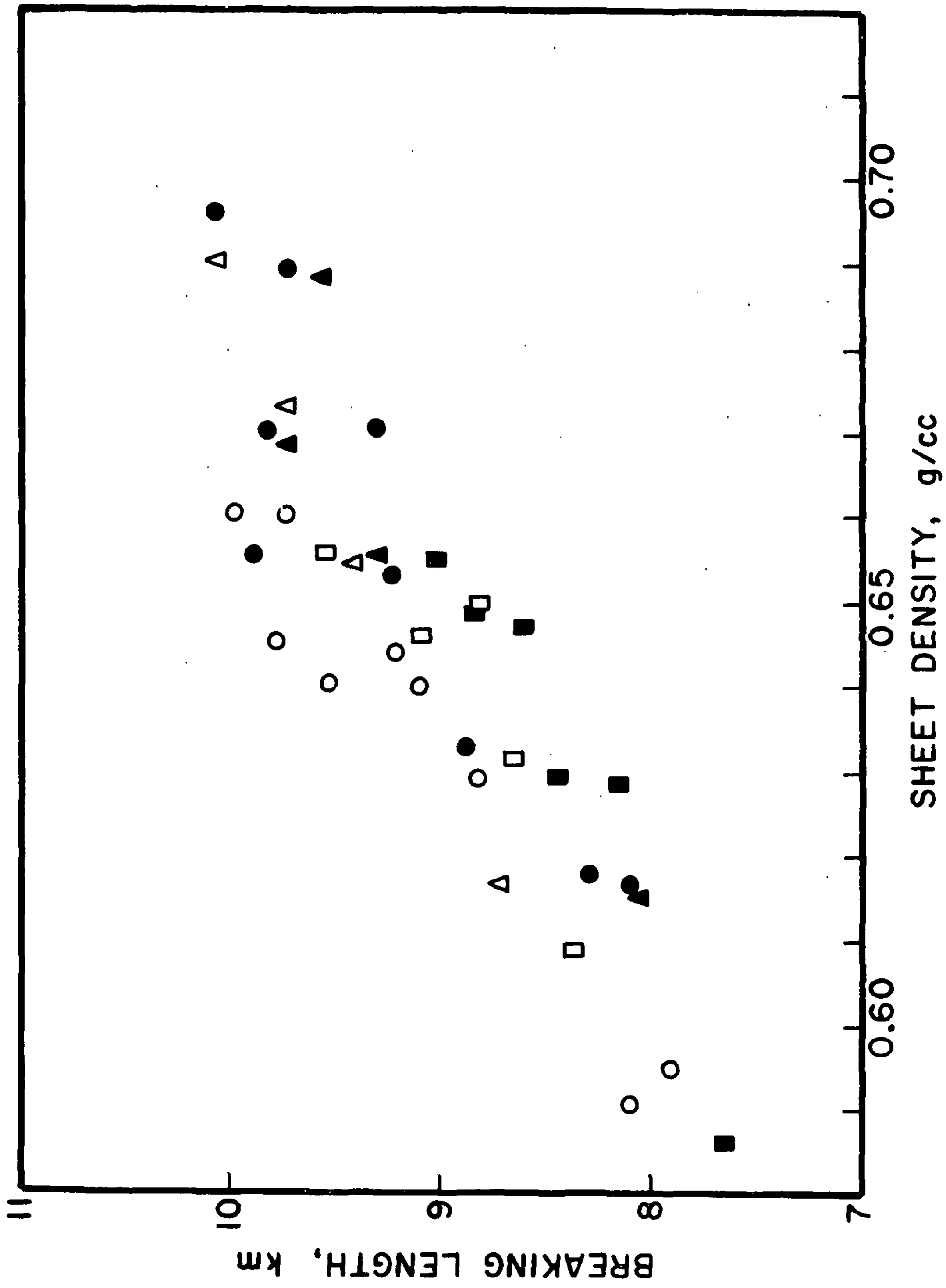

Figure 24. Tensile Strength vs. Sheet Density for Unbleached Pulps
Key to Symbols: Same as Figure 22

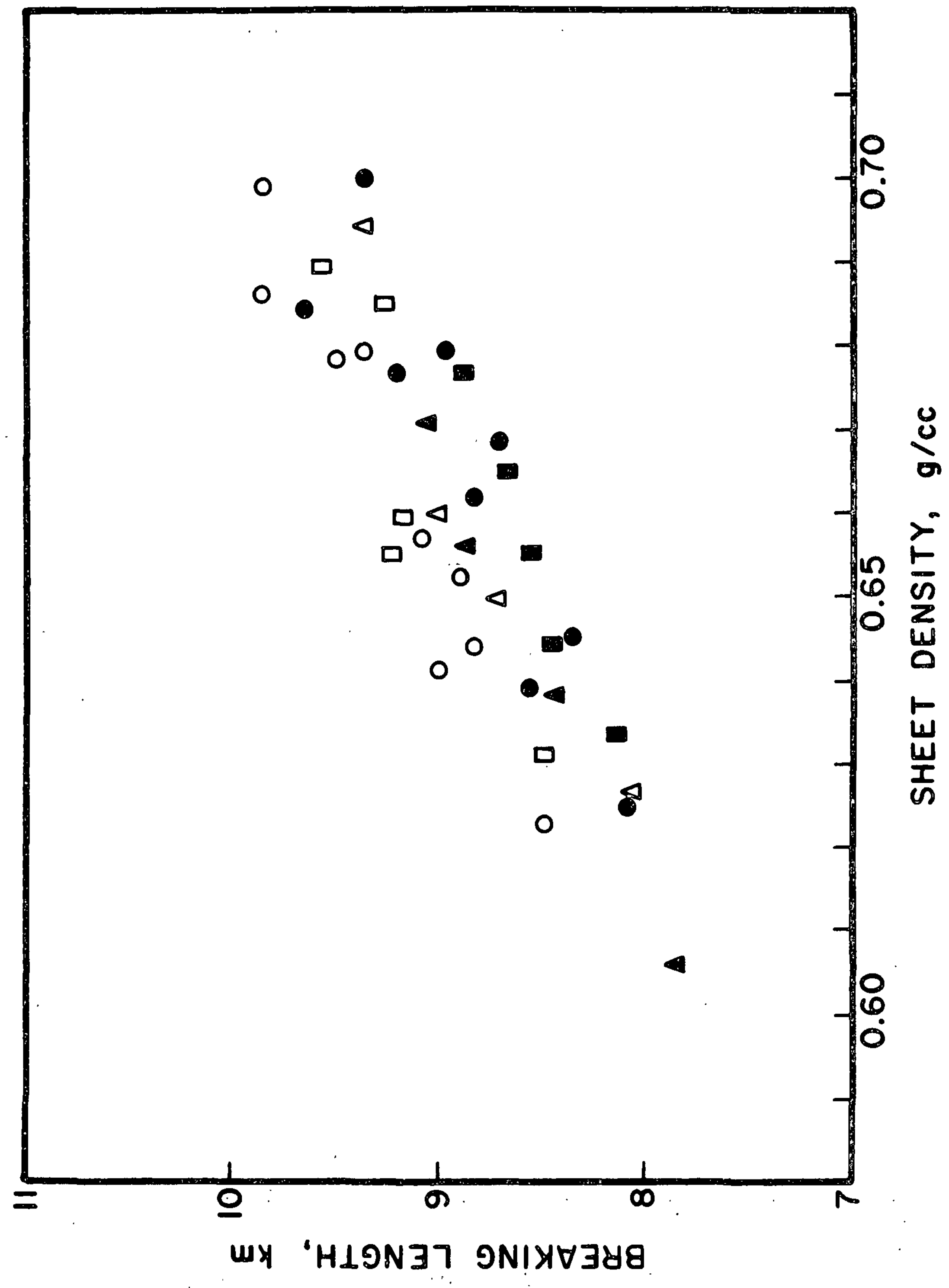

Figure 25. Tensile Strength vs. Sheet Density for Bleached Pulps
Key to Symbols: Same as Figure 22

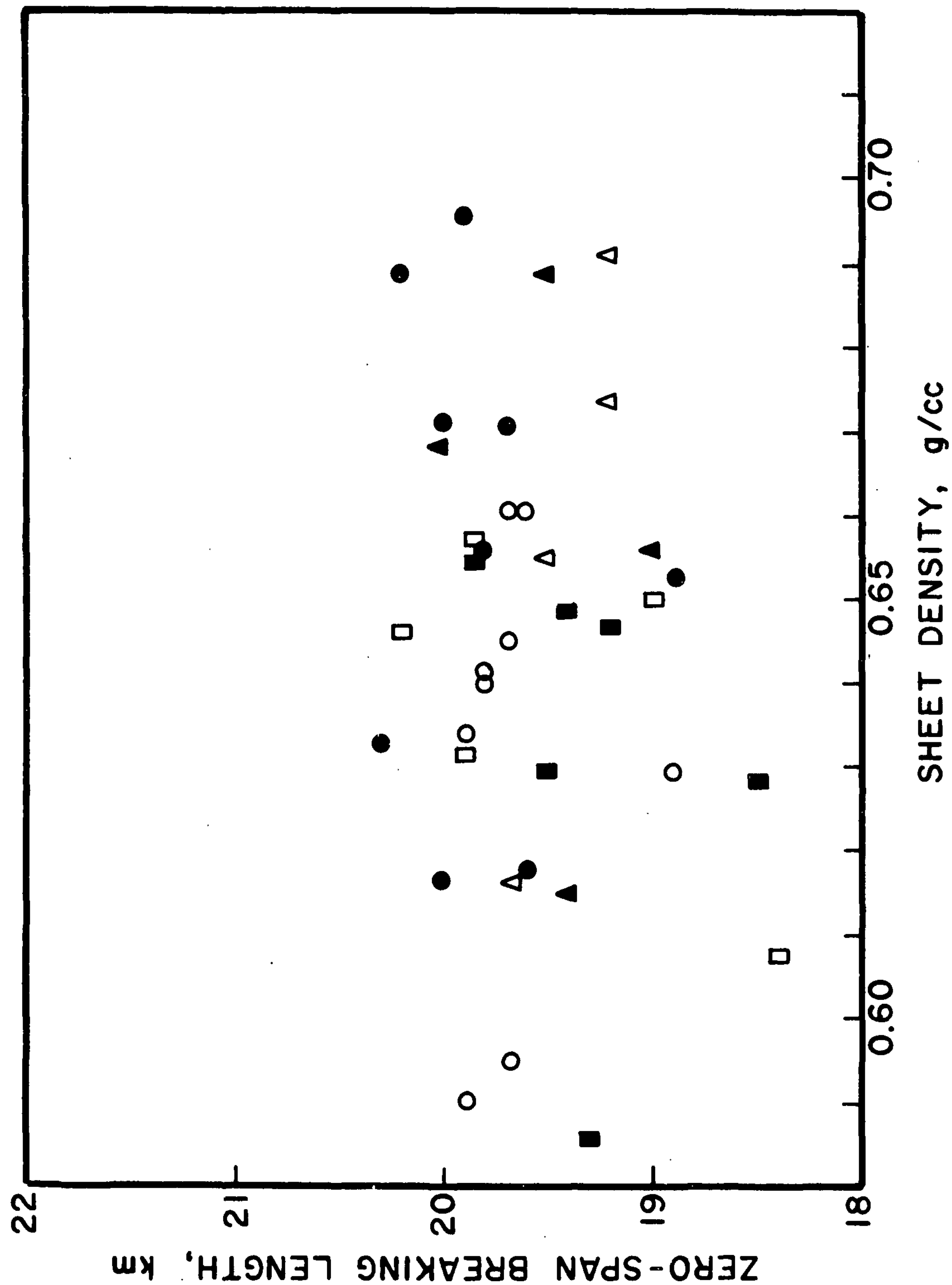

Figure 26. Zero-Span Tensile vs. Sheet Density for Unbleached Pulps
Key to Symbols: Same as Figure 22

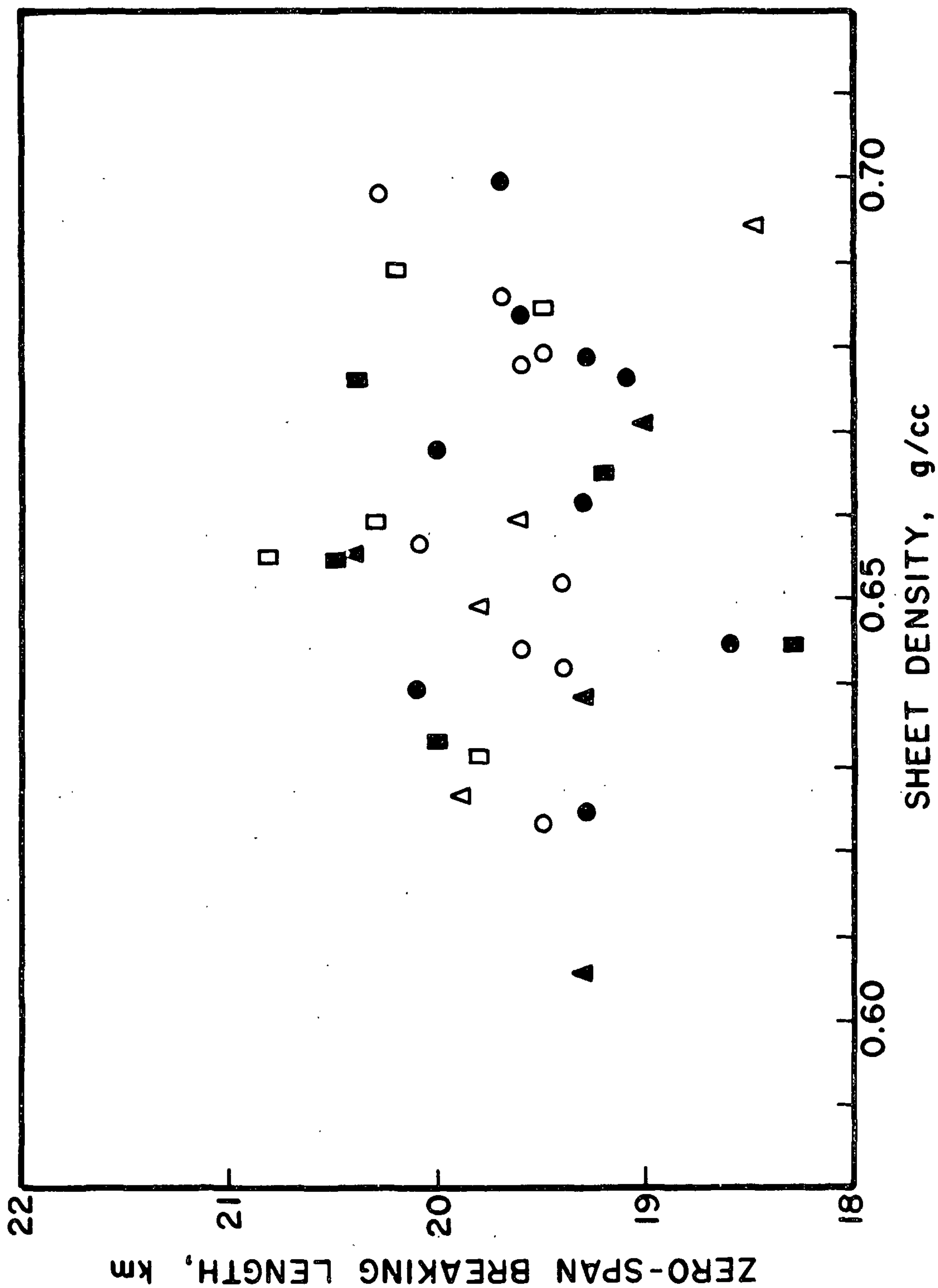

Figure 27. Zero-Span Tensile vs. Sheet Density for Bleached Pulps
Key to Symbols: Same as Figure 22

EXPERIMENTAL

PULPING

Southern pine logs were hand barked and chipped in a Carthage chipper. The chips were subsequently screened and the fraction passing through a 3/4-inch screen and retained on a 1/4-inch screen was used in the pulping experiments. The chips were air dried for storage prior to use.

Pulping runs were carried out in stainless steel bombs of 500-mL capacity which were heated by rotating them in a temperature-controlled oil bath. Prior to cooking, the chips were placed, together with the required amount of dilution water, in the bombs, which were then capped and allowed to stand overnight. Appropriate amounts of solutions of NaOH and Na_2S were added, together with anthraquinone if required.

After loading, the bombs were placed in the oil bath, which had been preheated to 60°C. Heating to the cooking temperature of 173°C lasted approximately 90 minutes. The temperature was closely monitored and the accumulated H-factor was calculated at intervals of 5-15 minutes. At the end of the required cooking time, the bombs were quickly cooled by successively spraying them with steam and cold water, opened, and the liquor was drained from the cooked chips. The chips were then fiberized for two minutes in a Waring Blendor to which 2000 mL of water had been added. If the pulp had been prepared for strength evaluations, a British disintegrator was used instead of the Waring Blendor and the disintegration time and volume of water added were, respectively, 5 minutes and 2 liters.

The fiberized pulps were subsequently washed by displacement in a sintered-glass filter funnel until the filtrate was colorless. They were then screened on a Valley Flat Screen equipped with a plate having 0.08-inch slots. The rejects were collected, dried, and weighed, and the accepts were dewatered, weighed, crumbed, and sampled for moisture determination after equilibrating overnight. The kappa number and viscosity of the accepted pulp were determined, and its yield was calculated.

BLEACHING

All bleaching was done in sealed polyester bags. Chemical charges and bleaching conditions are given as footnotes to the appropriate data tables.

PULP TESTING

Kappa number, viscosity, brightness, and strength testing were carried out according to the TAPPI Standard Methods. Viscosities of unbleached pulps were determined without prior treatment of the pulp except when the kappa number was 40 or greater. In these cases the pulps were delignified by allowing 1 g of pulp to stand overnight at ambient temperature in 10 mL of a solution containing 0.5 g $NaClO_2$ and 0.1 mL of glacial acetic acid.

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THE INSTITUTE OF PAPER CHEMISTRY

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APPENDIX

Figures 28-35 illustrate the effects of changing each of the pulping variables studied in the kraft system, as predicted by the polynomial model. In each case the continuous independent variable is time, and a second independent variable is the parameter. The other independent variables are held at their average (central) values.

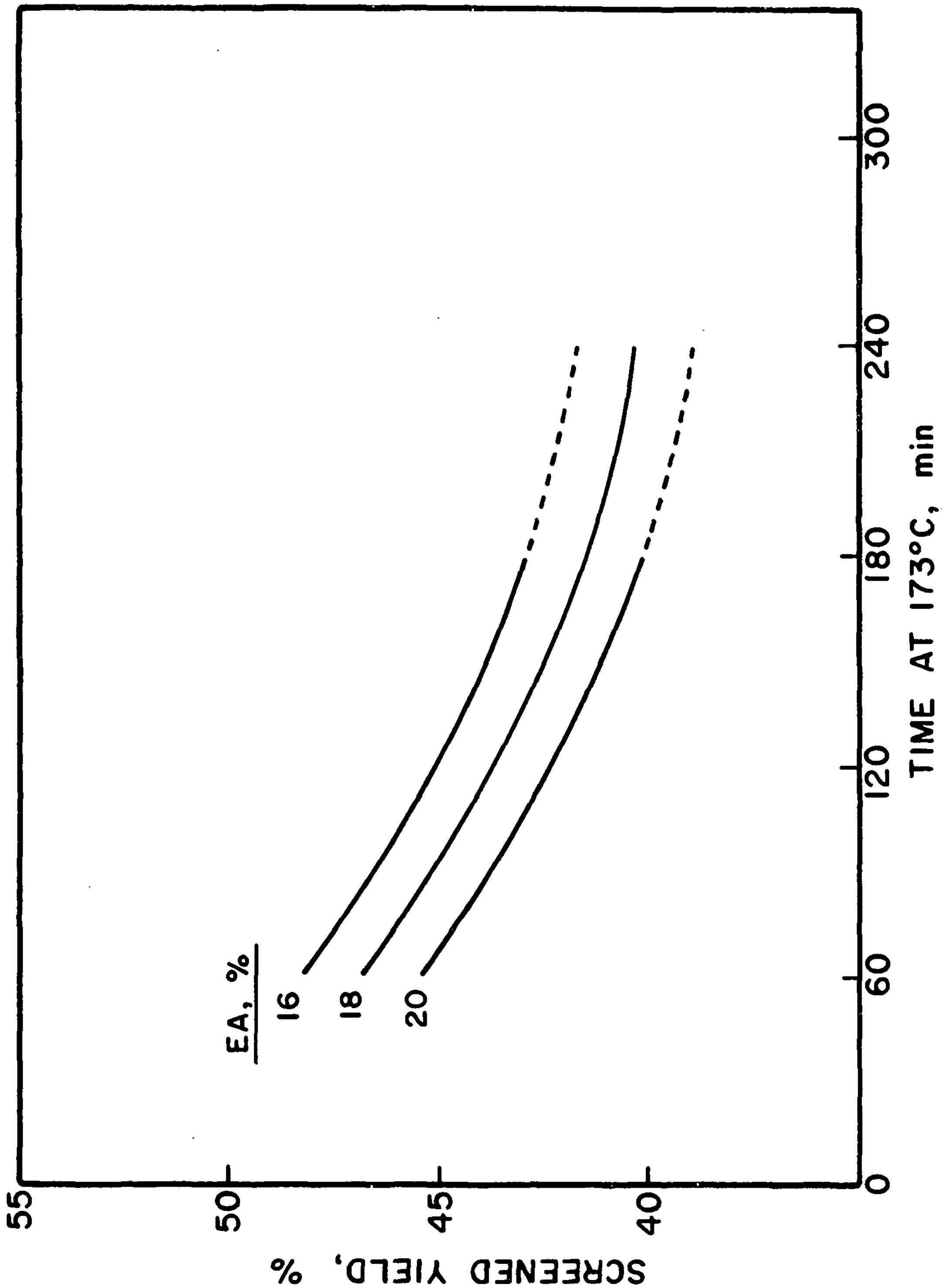

Figure 28. Effect of Effective Alkali Charge (EA) on Rate of Yield Loss in Kraft Pulping

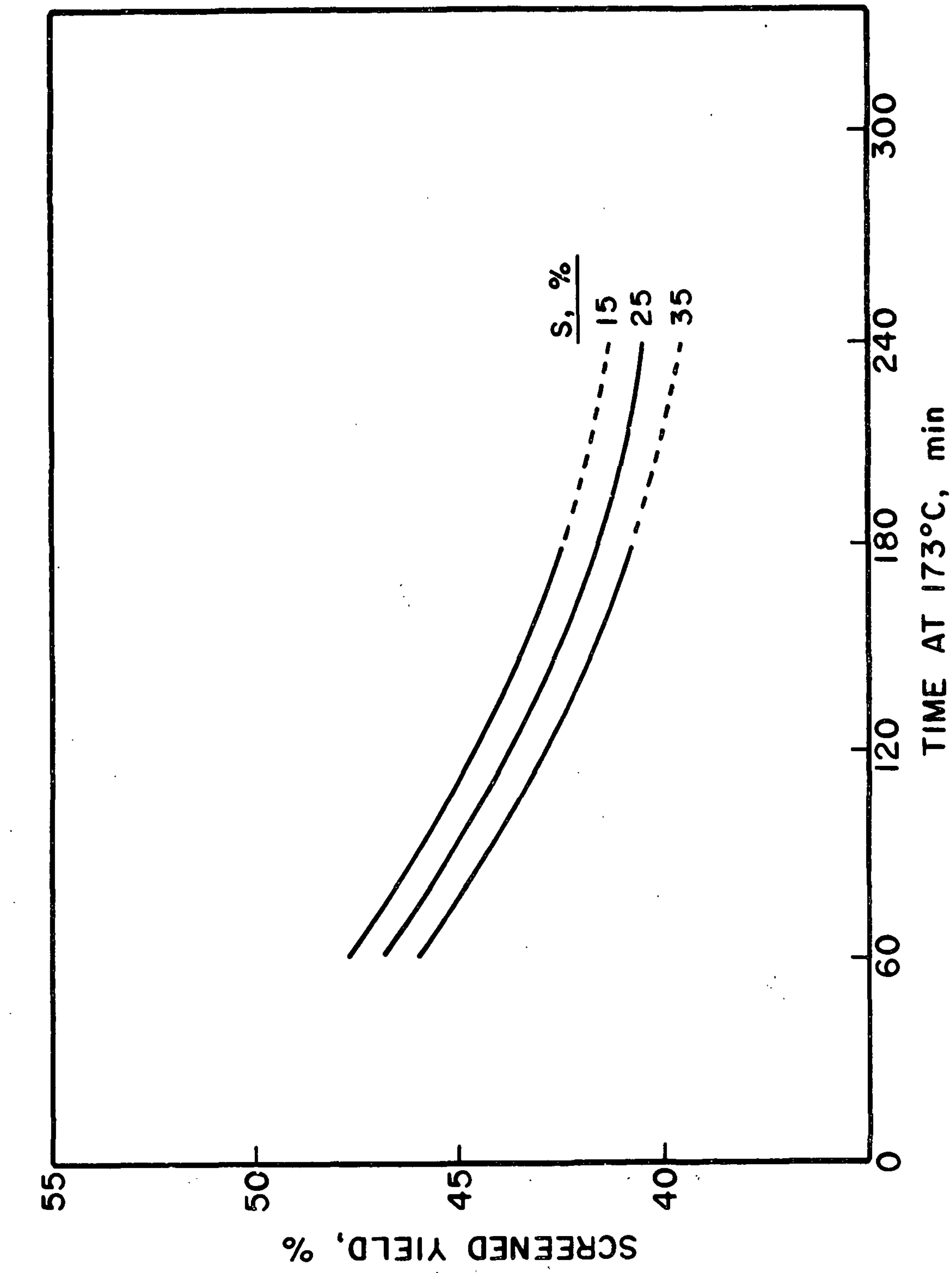

Figure 29. Effect of Sulfidity (S) on Rate of Yield Loss in Kraft Pulping

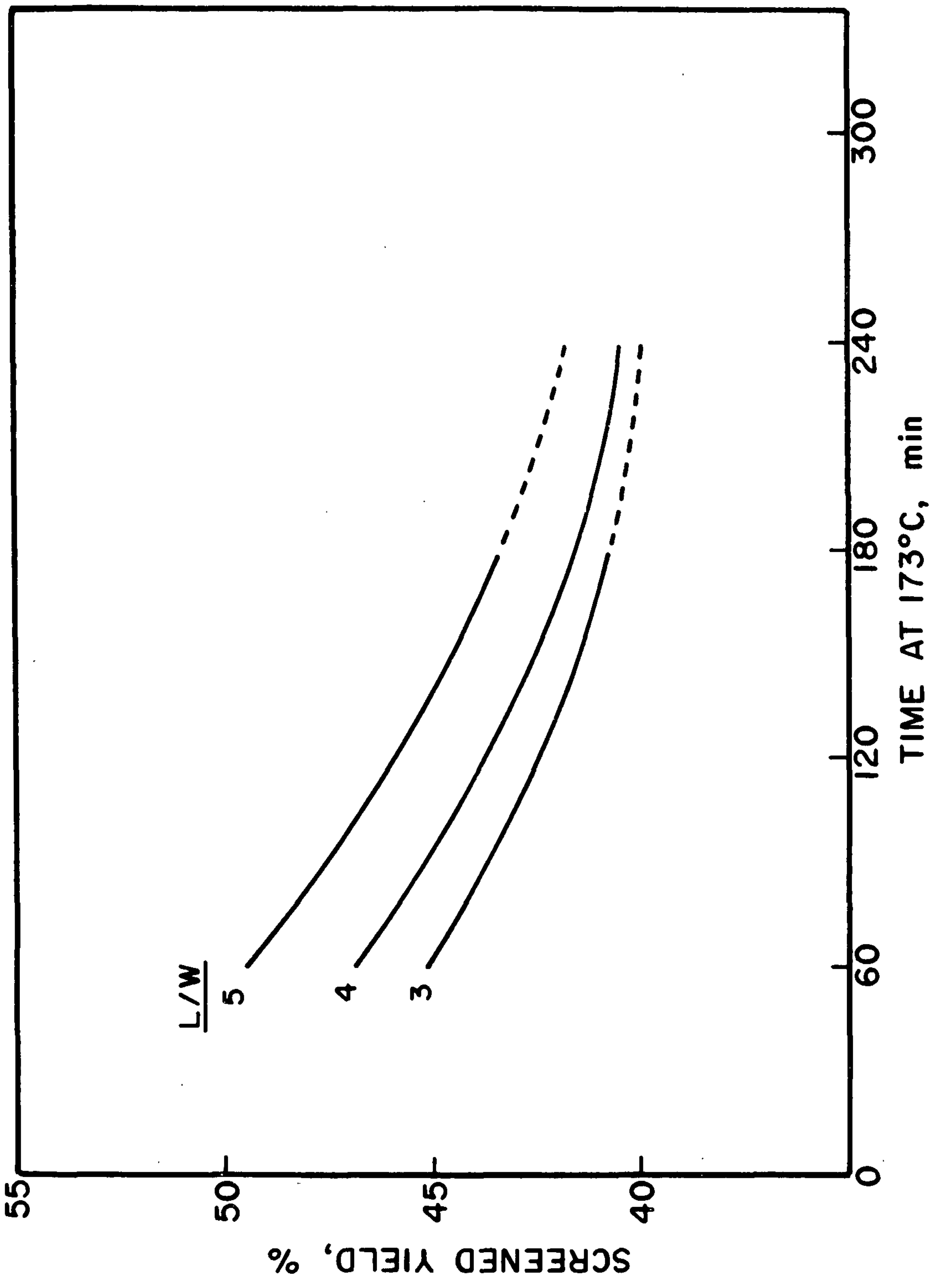

Figure 30. Effect of Liquor-to-Wood Ratio (L/W) on Rate of Yield Loss in Kraft Pulping

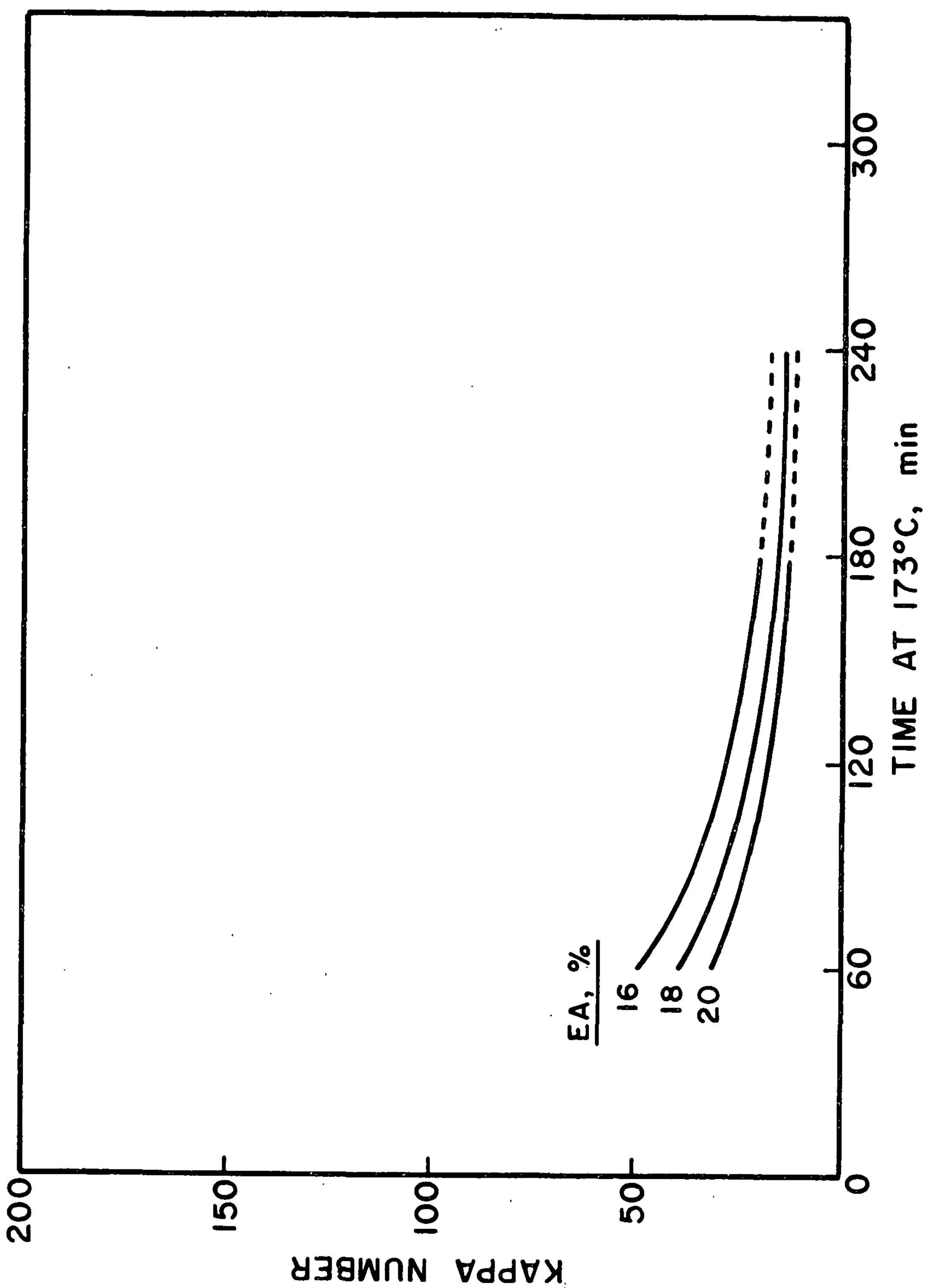

Figure 31. Effect of Effective Alkali Charge (EA) on Delignification Rate in Kraft Pulping

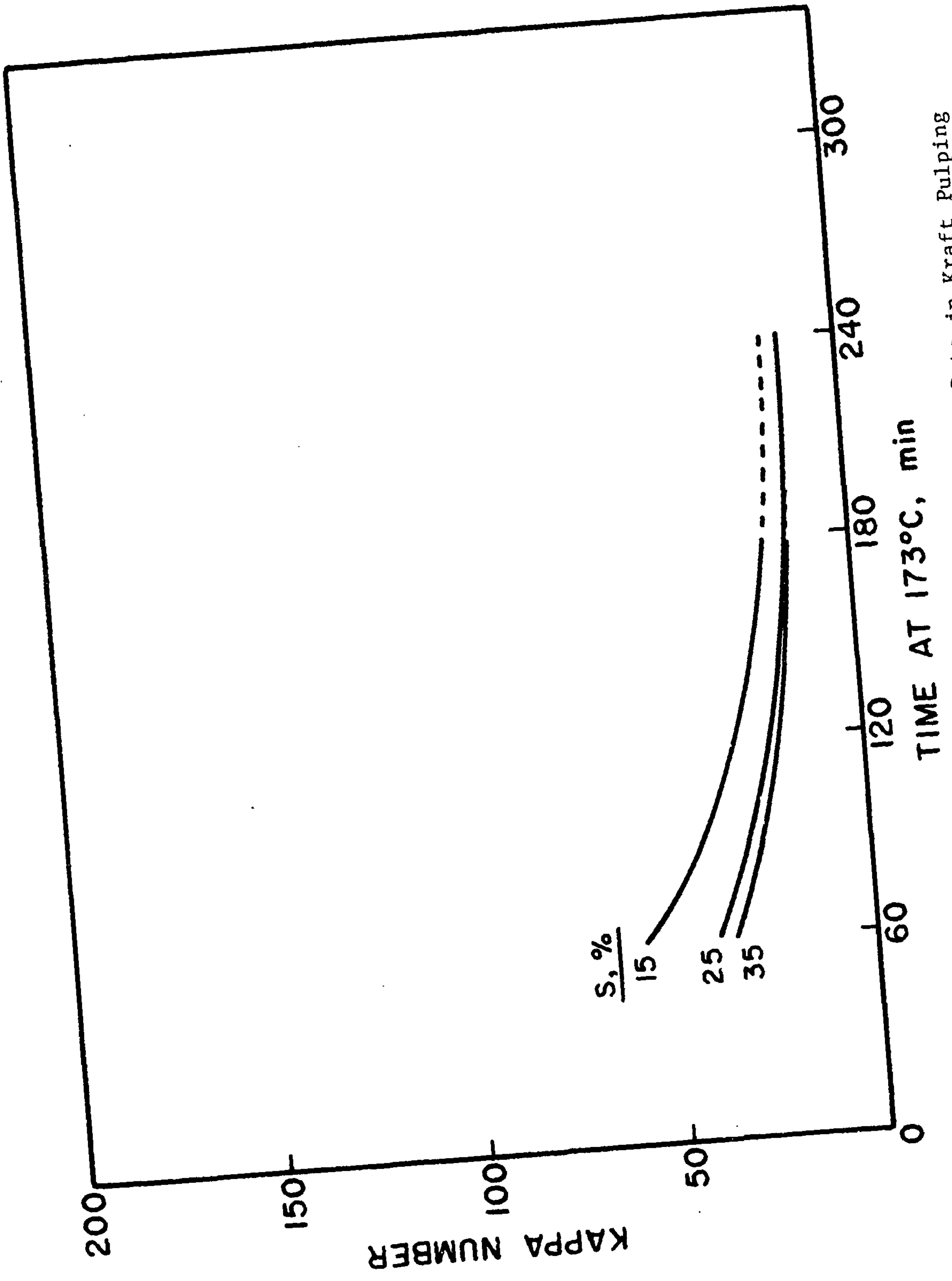

Figure 32. Effect of Sulfidity (S) on Delignification Rate in Kraft Pulping

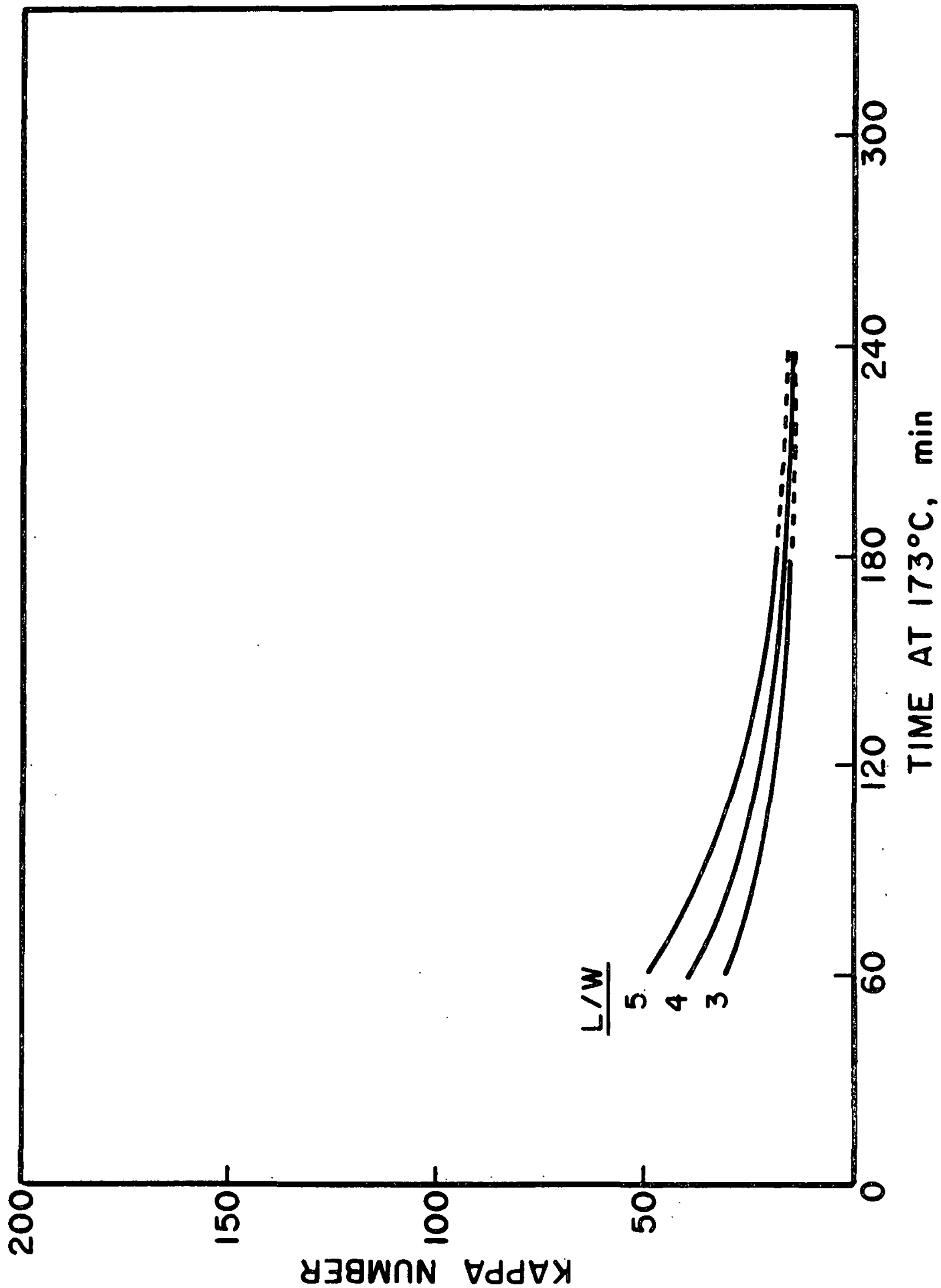

Figure 33. Effect of Liquor-to-Wood Ratio (L/W) on Delignification Rate in Kraft Pulping

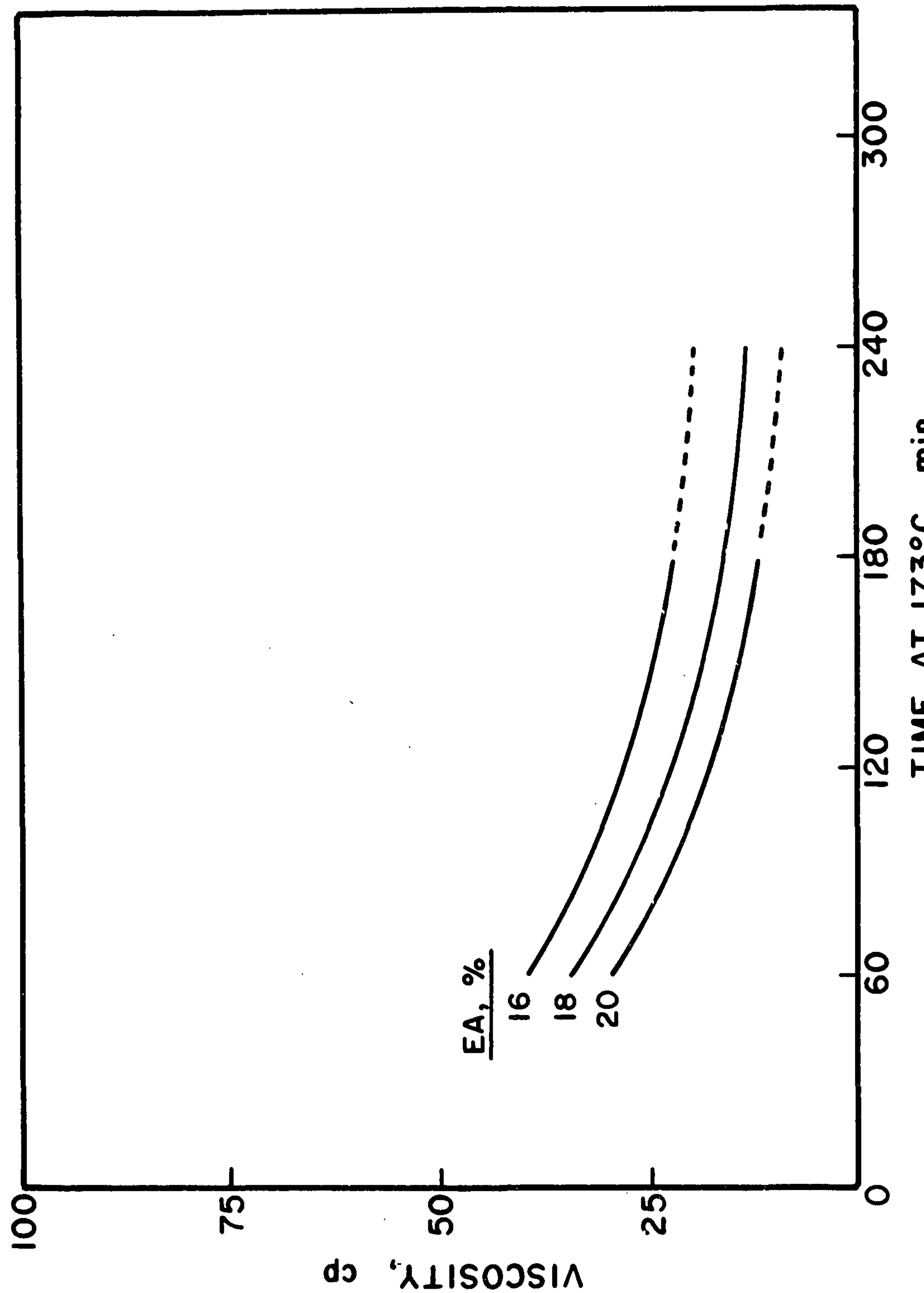

Figure 34. Effect of Effective Alkali Charge (EA) on Rate of Viscosity Loss in Kraft Pulping

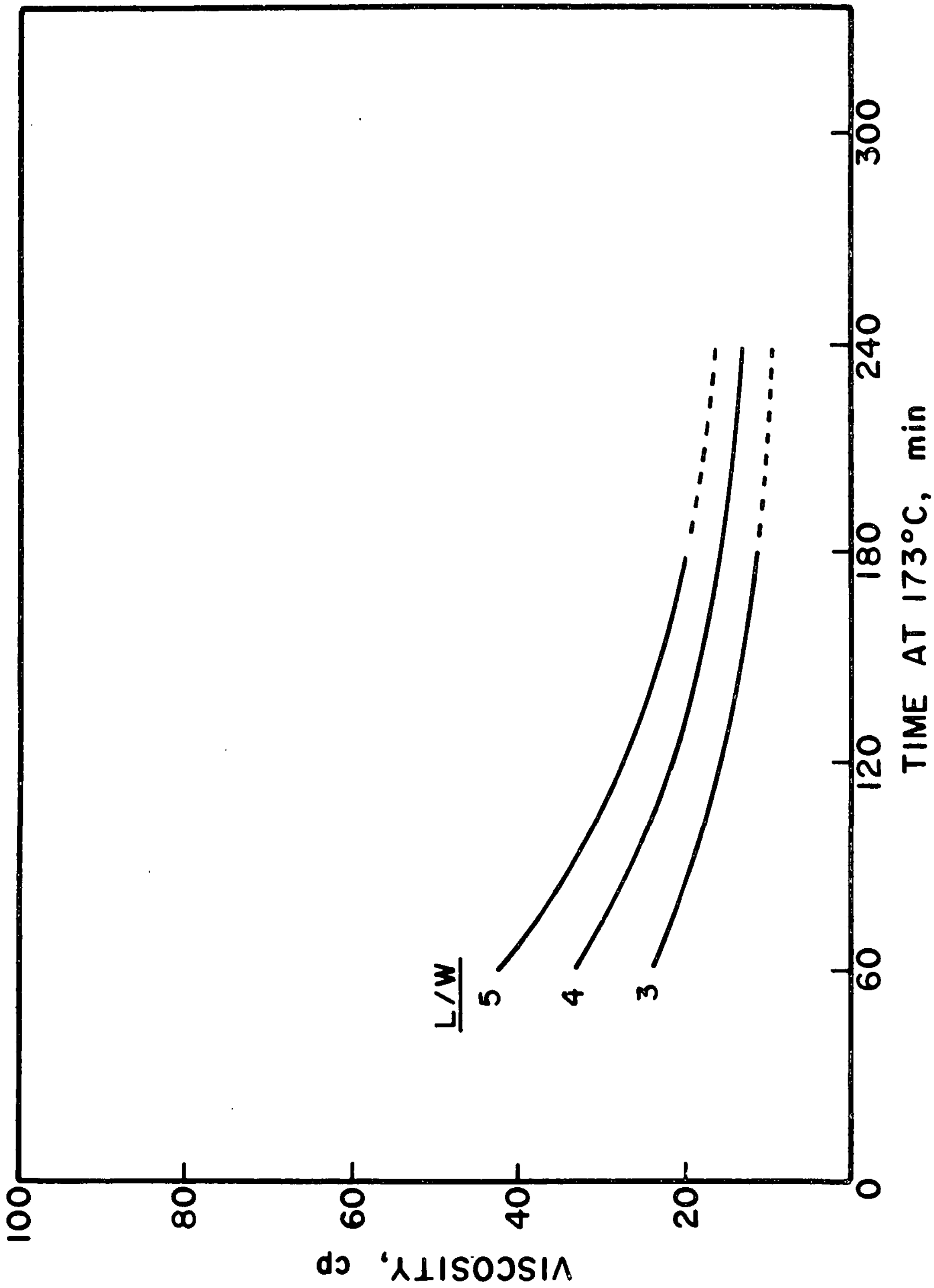

Figure 35. Effect of Liquor-to-Wood Ratio (L/W) on Rate of Viscosity Loss in Kraft Pulping